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Factors in Assessing the Compatibility of FMLs (Flexible Membrane Liners) and Waste Liquids

Matrecon, Inc., Alameda, CA

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16. ABSTRACT

This experimental research project studied various factors in the compatibility of flexible membrane liners (FMLs) with waste liquids and other hazardous substances that may be encountered in waste storage and disposal facilities. This work included: (1) Swelling of FMLs and other FML-related compositions in organics, and calculation of the solubility parameters of these compositions, (2) Distributions of organics between aqueous solutions, such as leachates, and FMLs, and (3) Variables in EPA Method 9090 compatibility testing of FMLs and waste liquids.

Equilibrium swelling of 28 FML-related polymeric compositions was determined in 30 organics and deionized water. The 30 organics covered a wide range of Hildebrand and component solubility parameters. Crystallinity of the polymers appears to dominate the swelling of an FML in organics and override the solubility parameters and crosslinking. Dissolved organics will transfer from a dilute aqueous solution to an FML that the solution is contacting and diffuse through to the FML's opposite side. The equilibrium ratio of the concentration of organics in an FML to that in an aqueous solution can vary over orders of magnitude, depending on the proximity of the solubility parameters of the organics and FMLs.

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FACTORS IN ASSESSING THE COMPATIBILITY OF FMLS AND WASTE LIQUIDS

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report presents the results of experimental investigations of various factors that contribute to the assessment and prediction of the compatibility of FMLs with waste liquids and other liquid substances that might be encountered in waste storage and disposal facilities. These investigations included:

1. Measurement of the swelling of 28 different polymeric FMLs and FML-type compositions in 31 different fluids covering a wide range of solubility characteristics.
2. Determination of the solubility parameters of the FMLs based on their swelling.
3. A study of the partitioning of dissolved organics between leachates and FMLs, and the transport of the organics through FMLs.
4. A study of the factors involved in the compatibility testing of FMLs and leachates and other liquids.

Thomas R. Hauser, Director
Hazardous Waste Engineering
Research Laboratory

ABSTRACT

This experimental research project studied various factors in the compatibility of flexible membrane liners (FMLs) with waste liquids and other hazardous substances that may be encountered in waste storage and disposal facilities. This work was conducted in three basic areas:

1. Swelling of FMLs and other FML-related compositions in organics, and calculation of the solubility parameters of these compositions.
2. Distribution of organics between aqueous solutions, such as leachates, and FMLs.
3. Variables in EPA Method 9090 compatibility testing of FMLs and waste liquids.

Equilibrium swelling of 28 FML-related polymeric compositions was determined in 30 organics and deionized (DI) water. These 28 polymeric materials included thermoplastic (TP), crosslinked (XL), and semicrystalline (CX) compositions, of which 22 were commercial FMLs or sheetings and six were known compositions prepared in the laboratory for this study. Basic polymer and compound variations (e.g. differences in polymer type, level of crystallinity, crosslink density, filler level, and amount and type of plasticizer) were assessed. The 30 organics covered a wide range of Hildebrand solubility parameters as well as the component solubility parameters.

Crystallinity of the base polymer appears to be the dominant factor in reducing the swelling of an FML or an FML-related composition in all of the organics and to override both the solubility parameters and crosslinking. Among compositions based on amorphous polymers, the proximity of the component solubility parameters to those of the organics could be used in most cases to indicate the swelling and the probability of changes in properties. Nevertheless, empirically derived data are still necessary for untested combinations of organics and FMLs.

Dissolved organics will transfer from a dilute aqueous solution to an FML with which the solution is in contact and will diffuse through to the opposite side of the FML. The equilibrium ratio of the concentration of organics in an FML to that in an aqueous solution can vary over orders of

magnitude, depending on the proximity of the solubility parameters of the organics and the FMLs. A multi-compartment test apparatus with FML specimens between the compartments appears to be an appropriate means of measuring the movement of organics from dilute solutions and measuring transmission through FMLs.

In conducting compatibility tests of waste liquids that contain volatile organics, it has been found necessary, in order to simulate the effects of actual exposure, to prevent the loss of these organics from the time the leachate is sampled in the field through the actual test of exposed FML specimens. The results indicate the desirability of changing the waste at the beginning of each month of testing in order to maintain concentrations of the organics.

This report was submitted in fulfillment of Contract No. 68-03-3213 by Matrecon, Inc. under the sponsorship of the U.S. Environment Protection Agency. This report covers the period from June 1984 through August 1987.

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ABBREVIATIONS AND SYMBOLS

ASTM	American Society for Testing and Materials
AM	Amorphous
BP	Boiling point
°C	Degree celsius
cal	Calorie
CASNO	Chemical Abstract Services' number
CED	Cohesive energy density
cm	Centimeter
CPE	Chlorinated polyethylene
CR	Chloroprene rubber (neoprene)
CSPE	Chlorosulfonated polyethylene
CX	Semicrystalline thermoplastic
d	Dispersion; day
δ_d	Dispersive solubility parameter
δ_o	Hildebrand solubility parameter
δ_h	Hydrogen-bonding solubility parameter
δ_p	Polarity solubility parameter
δ_t	Total solubility parameter
δ	Solubility parameter
db	On a dried basis
DEHP	Di(ethylhexyl) phthalate
DI	Deionized water

D_{LW}	Distribution between FML and water
DSC	Differential scanning calorimetry
ECO	Epichlorohydrin rubber
EPDM	Ethylene propylene rubber
ELPO	Elasticized polyolefin
EPA	U.S. Environmental Protection Agency
epi	Ends per inch
ESC	Environmental stress-cracking
EVA	Ethylene vinyl acetate
°F	Degree fahrenheit
FML	Flexible membrane liner
FSOT	Fused silica open tube
ft	Foot
FTMS	Federal Test Method Standard
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectroscopy
g	Gram
gal	Gallon
h	Hour; hydrogen bonding
He	Helium
HDPE	High-density polyethylene
HDPE-A	HDPE/ethylene propylene rubber alloy
HSGC	Headspace gas chromatography
IIR	Butyl rubber
in.	Inch

ipm	Inches per minute
L	Liter
lb	Pound
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MEK	Methyl ethyl ketone
mg	Milligram
mil	Inch x 0.001
min	Minimum
min.	Minute
mL	Milliliters
μL	Microliter
mm	millimeters
μm	Micrometer
MP	Melting point
N	Normal
na	Not applicable
NBR	Nitrile rubber
oz	Ounce
p	Polarity
PCB	Polychlorinated biphenyls
PB	Polybutylene
PE	Polyethylene
PEL	Polyester elastomer
PP	Polypropylene
ppi	Pounds per inch

ppm	Parts per million
psi	Pounds per square inch
PU	Polyurethane
PVC	Polyvinyl chloride
PVC-E	Polyvinyl chloride (elasticized)
PVC-OR	Polyvinyl chloride (oil resistant)
QA	Quality Assurance
QC	Quality Control
R	Fabric reinforced
RCRA	Resource Conservation and Recovery Act
R_d	Range value for dispersive solubility parameter
R_h	Range value for hydrogen-bonding solubility parameter
R_p	Range value for polarity solubility parameter
sq	Square
S-100	Stress at 100% elongation
S-200	Stress at 200% elongation
TBP	Tri-n-butyl phosphate
TCA	1,1,1,-Trichloroethane
TCE	Trichloroethylene
TDS	Total dissolved solids
TGA	Thermogravimetric analysis
TP	Thermoplastic polymeric composition
XL	Crosslinked polymeric composition

METRIC CONVERSION FACTORS

(U.S. Customary Units to SI Units)

To convert	Multiply by
Inches to centimeters (cm)	x 2.54
Feet to meters	x 0.3048
Mils to centimeters (cm)	x 2.54×10^{-3}
Mils to millimeters (mm)	x 2.54×10^{-2}
Pounds per square inch (psi) to megapascals (MPa)	x 6.895×10^{-3}
Pounds per inch (ppi) to kilonewtons per meter (kN/m)	x 1.751×10^{-1}
Pounds (force) to Newtons	x 4.448

U.S. Customary Units are used in this report as they are commercially used in the United States in the solid wastes industry as well as in the liner production and installation industries.

SECTION 1

INTRODUCTION

The compatibility of a proposed polymeric membrane liner with the waste to be contained is a principal requirement of the Resource Conversation and Recovery Act (RCRA) permitting process for the construction of a waste storage and disposal facility. The other principal requirements are low permeability and durability. Thus, a liner material must have low permeability to all the constituents of a waste liquid and must maintain its physical integrity, including seams, to contain the particular waste effectively for the required length of time. These requirements may be for extended periods of time, e.g. as in landfills, or they may only be for a few years, e.g. in an evaporation pond.

The technology involving the use of polymeric membranes for lining storage and disposal facilities is relatively new. At present, information in the open literature regarding the compatibility of flexible membrane liners (FMLs) and waste liquids based on actual experience continues to be limited. On the other hand, considerable information regarding the compatibility of specific polymeric materials with specific organics and liquids is available which the engineer and designer can use to assess potential compatibility of given materials with given waste liquids. Because waste liquids can be complex mixtures with the possibility of detrimental effects due to the combination of components, the compatibility of a lining material with a specific waste liquid needs to be determined. Reliable test protocols are needed so that correct assessment of the liner-waste compatibility can be made by the permit writer when reviewing a permit application.

In assessing the suitability of a polymeric product designed to be in contact with liquids and chemicals, it is common practice in the rubber and plastics industries to use solubility parameters to select the polymer compound and ultimately to expose the composition to the liquid with which it is to be in contact (Beerbower et al, 1967). The effects of the exposure upon the physical properties of the compositions are measured as a function of time. The swelling and dimensional changes that take place and the changes in mechanical properties, such as tensile strength, elongation at break, tear strength, and modulus are normally measured. For many applications service life is estimated as the time to a percentage change in a property relevant to its performance or one that has been correlated with performance.

In rubber technology, compositions that lose or gain 15 points in hardness often are considered to have failed. Other criteria of failure or limits of serviceability often used are 50% increase or loss in modulus, or 50% losses in tensile strength or elongation at break, or a certain amount of swelling which would change dimensions and result in nonfunctioning of a product or part. However, these levels of maximum change have been correlated with experience with specific products in simulated service tests or in actual service. In the case of FMLs used in lining waste storage and disposal facilities, specific criteria for an allowable magnitude of change in specific properties beyond which an FML "fails" have not been developed.

Among properties that appear to be related to FML performance, the swelling or loss in weight in service is one of the most useful tools in assessing its compatibility with wastes. Associated with these changes in weight are changes in most of the physical properties, such as tensile strenth, tear strength, modulus, hardness, permeability, puncture resistance, and fatigue resistance.

Matching the solubility parameter values of an FML with those of a specific waste liquid and its constituents has been suggested as a means of predicting the swelling that might take place in an FML on exposure [Haxo, 1981; Matrecon, 1983 (p 177)]. Applicability of the solubility parameter values concept to estimate the compatibility of FMLs and specific wastes and to estimate the service lives of FMLs, however, had not been quantified; this was one of the principal objectives of this project.

In addition to the possible use of solubility parameters for predicting compatibility and service lives of FMLs as liners in specific waste storage and disposal facilities, there are several other factors which can affect the magnitude of swelling and possibly the ultimate service life. The compositional factors include:

- Degree of crystallinity of the polymer.
- Level of crosslinking of the polymer.
- Amount of filler in the compound formulation.
- Amount of plasticizer in the compound.
- Amount of waste soluble constituents in the compound.

The environmental factors include:

- Concentration of the organics and the partitioning of an organic dissolved in the waste liquid with a polymeric liner.
- The effect of strain or stress on a liner in service.

This project was undertaken to investigate and quantify the various factors that contribute to the performance of FMLs and their compatibility with waste liquids in waste storage and disposal facilities and to investigate factors involved in predicting long-term compatibility and service life.

SECTION 2

OBJECTIVES

The four principal objectives of this project were:

- To develop a methodology that can be used to predict the compatibility of FMLs with specific waste liquids and to estimate their service lives for lining waste storage and disposal facilities.

- To determine the solubility parameters of polymeric FMLs and to explore their use for determining the compatibility of FMLs with waste liquids of different types.

- To assess the different factors that affect the magnitude of swelling of an FML in contact with waste liquids.

- To determine the effects of swelling on mechanical and permeability characteristics of FMLs in service.

In addition to the above, this project had the following secondary objectives:

- To assess the effects on polymeric FMLs of organics in dilute solutions and determine whether threshold levels for organic species in waste liquids can be set.

- To assess the effects on polymeric FMLs of exposure to waste liquids, such as in the testing of environmental stress-cracking resistance.

- To determine the importance of crosslink type and crosslink density upon FML behavior in waste impoundment environments.

- To determine the applicability of higher exposure temperatures in performing compatibility tests and in estimating the service life of an FML as a liner in a waste storage and disposal facility.

SECTION 3

SUMMARY AND CONCLUSIONS

The work conducted on this project was in three major areas relating to the chemical compatibility of FMLs with waste liquids and leachates:

- Swelling of FMLs in organics and calculations of the solubility parameters of the FMLs and related compositions.
- Distribution of organics in aqueous solutions between water and FMLs.
- Study of variables in FML/waste liquid compatibility testing.

This section summarizes the work and presents conclusions.

SWELLING OF FMLS IN ORGANICS AND CALCULATIONS OF THE SOLUBILITY PARAMETERS OF THE FMLS AND RELATED COMPOSITIONS

Equilibrium swelling of 28 FML-related polymeric compositions was determined in 30 organics and deionized (DI) water. These 28 polymeric materials included thermoplastic (TP), crosslinked (XL), and semicrystalline (CX) compositions, of which 22 were commercial FMLs or sheetings and six were laboratory-prepared compositions. Within these 28 compositions, basic polymer and compound variations were included, such as polymer types, level of crystallinity, crosslink density, filler level, and amount and type of plasticizer.

The 30 organics covered a wide range of Hildebrand solubility parameters as well as the component solubility parameters, i.e. the dispersive (δ_d), polarity (δ_p), and hydrogen-bonding (δ_h) components. The organics were selected by a computer program from a list of 131 organics on which the solubility parameter data were available and which covered the ranges of component solubility parameter values, as well as the Hildebrand parameter.

Equilibrium swelling was measured by weighing specimens of polymeric compositions that had been immersed in the individual neat organics until there was essentially no change in weight. Each of the solubility parameters, including the Hildebrand and component parameters, were then calculated from the swelling data for each of the polymeric compositions through a computer program which generated the curve that best fit the data for that parameter.

The most significant results of this swelling study were:

- The crystallinity of the polymer appeared to be the dominant factor in reducing the swelling of a polymeric composition in all of the organics and appeared to override both the crosslinking and the solubility parameters.
- The crosslinking of an amorphous polymer reduced swelling in all of the organics compared with the uncrosslinked polymer. Increasing the crosslinking density reduced the swelling.

  Note: The crystallinity and crosslinking factors are not additive. The introduction of crosslinking in semicrystalline polymeric compositions tends to reduce the amount of crystallinity.

- Though the magnitude of swelling of amorphous polymers could, in many instances, be estimated from the proximity of the values of the component solubility parameters of the polymer and those of the organic, the swelling of the FML in many combinations could only be roughly estimated based upon the type of organic. The matching of the Hildebrand solubility parameter values remains a necessary, but not sufficient condition for swelling. The swelling tests should be performed to ensure that an amorphous FML will not swell in a particular organic. Thus, empirically derived data are still needed for untested combinations of organics and FMLs.
- With waste liquids that contained dissolved organics, the organics were absorbed by the FML; the amounts absorbed depended on: (1) the relationship of the solubility parameters of the organic and the FML; and (2) the solubility of the organic in water.

DISTRIBUTION OF ORGANICS IN AQUEOUS SOLUTIONS BETWEEN WATER AND FMLS

A series of experiments was performed to study the distribution of organics from dilute aqueous solutions to FMLs and the permeation of these organics through the FMLs. Three preliminary experiments were performed to explore the movement of organics with respect to water and FMLs and to assess gas chromatography as a means of measuring the concentrations of organics so that their movement from one solution into another could be followed. These experiments were as follows:

- Measurement of the distribution of seven organics in mixtures at different ratios with water between the organic phase and water. The mixtures included organics having a wide range of solubilities in water from miscibility to almost complete insolubility.

- Measurement of the distribution of organics between water and a paraffinic oil which was selected to simulate polyethylene because of their chemical similarity.

- Measurement of the distribution of organics in a dilute aqueous solution of organics and a high-density polyethylene (HDPE) FML which was immersed in the solution.

A series of six additional and more extensive experiments were conducted to assess the distribution of organics between water and FMLs:

- To determine the distribution of organics between saturated aqueous solutions of individual organics and a polyethylene FML.

- To determine the distribution of organics between organic-saturated FML specimens and DI water.

- To determine, in a two-compartment test apparatus, the distribution and transmission of nine organics in a dilute aqueous solution through a linear low-density polyethylene (LLDPE) FML.

- To determine, in the two-compartment test apparatus, the distribution of trichloroethylene (TCE) in a dilute aqueous solution among the airspaces, the water layer, and the FML separating the two compartments.

- To determine, in a vapor-tight three-compartment test apparatus, the distribution of the trichloroethylene and toluene from a dilute solution to the vapor, water, and FML layers.

- To determine the distribution, in the three-compartment test apparatus separated by polyethylene (PE) FMLs, of six volatile organics initially in a dilute aqueous solution. These organics covered the range of solubility parameters from an alkane to an organic acid.

The results of these experiments demonstrated that the organics, based upon their solubility parameters, will transfer from a dilute aqueous solution to the FML with which the solution is in contact and, if volatile, permeate into the airspace on the opposite side of the FML as a vapor. The ultimate ratio, at equilibrium, of the concentration of the organics in the FML to that in the water can vary over hundreds of orders of magnitude, depending on the solubility parameters of the organics.

A multi-compartment test apparatus with FML specimens between the compartments to simulate the condition of a waste liquid in service appears to be an appropriate means of measuring the movement of organics from dilute solutions and transmission through FMLs. The concentration of the organics in the various zones of the test apparatus can be followed by gas chromatographic (GC) analysis of the vapors and liquids and headspace gas chromatographic (HSGC) analysis of the FML.

The solubility of an organic in water appears to have been a significant factor in its movement through the apparatus. For example, n-octane, when added to water in the three-compartment test apparatus, tended to volatilize and be transported into the airspace above the top FML rather than into the lower FML and the airspace below the dilute aqueous solution of organics. TCE, which is highly volatile and yet has a relatively high solubility in water, was transmitted relatively fast throughout the three compartments of the test apparatus, thus showing its high mobility.

Considerable time was required for the organics originally in the dilute solution in the apparatus to reach equilibrium in the vapor, the water, and the FMLs layers. This indicates the need for relatively long exposure periods, e.g. four months, for conducting compatibility tests of FMLs in dilute solutions and waste liquids. Because of the long exposure period, vapor-tight exposure tanks should be used.

STUDY OF VARIABLES IN FML/WASTE LIQUID COMPATIBILITY TESTING

In view of the complexity of the EPA Method 9090 (EPA, 1984 and 1986), a desire to improve the long-range reliability of the test and, if possible, to shorten the length of the test, a series of experiments was performed to assess various factors that might affect the test results.

Two EPA Method 9090-type tests were performed with a polyethylene FML. The first tested the FML with a landfill leachate spiked with five organics (two chlorinated and three aromatic), and the second test was performed with DI water spiked with 11 organics representing a range of volatilities and solubility parameters. These tests were performed in tanks constructed of 316 stainless steel designed to prevent loss of volatiles. The test with the spike containing 11 organics was performed in duplicate and at two temperatures (23° and 50°C) for the four months of exposure required by EPA Test Method 9090. The concentrations of the organics in the liquid were monitored during the exposure part of the test and the FMLs were analyzed by headspace GC at the end of each exposure period.

In addition to the immersion tests, experiments were performed on dilute aqueous solutions of organics and organic-saturated FMLs to demonstrate the rapid rate at which the volatiles can be lost from waste liquids that contain volatiles if not properly protected. The loss of volatiles from aqueous solutions of single volatile organics shows the need for adequate control in sealing the leachate that is recovered from the field for testing. Although not as rapid a loss as encountered with the aqueous solutions of volatile organics, the loss of volatiles from exposed FMLs prior to test could also be significant.

At the higher temperatures (50°C) the losses of volatiles were significantly greater than those at 23°C. However, the effect of temperature on the test results was not apparent due to the high loss of volatiles in both cases. The loss of volatiles after spiking with the organics was essentially complete at the end of the four months of exposure, in spite of the Teflon gaskets that were added to seal the exposure tanks. The replenishment of the waste liquid during the exposure testing appears to be essential.

The nonvolatile constituents, tri-n-butyl phosphate (TBP) and di(ethylhexyl) phthalate (DEHP), of the spike continued to be absorbed during immersion as shown by increased extractables of the exposed FMLs.

The results for the duplicate exposures were in agreement, which indicates that the EPA Method 9090 liner/waste compatibility test can be reproducible.

Overall, these experiments demonstrate that the volatile organics need to be highly controlled during all phases of a compatibility test. In order to simulate actual exposure, great care must be taken to prevent losses of volatiles from a leachate that contains volatile organics from the time the leachate is sampled in the field through the actual testing of the exposed FML specimens.

SECTION 4

BACKGROUND

WASTE LIQUIDS IN CONTACT WITH POLYMERIC LINERS

Two conditions that could be encountered by an FML in contact with waste liquids that contain organics, either dissolved in water or in mixtures of organics, are schematically illustrated in Figure 1.

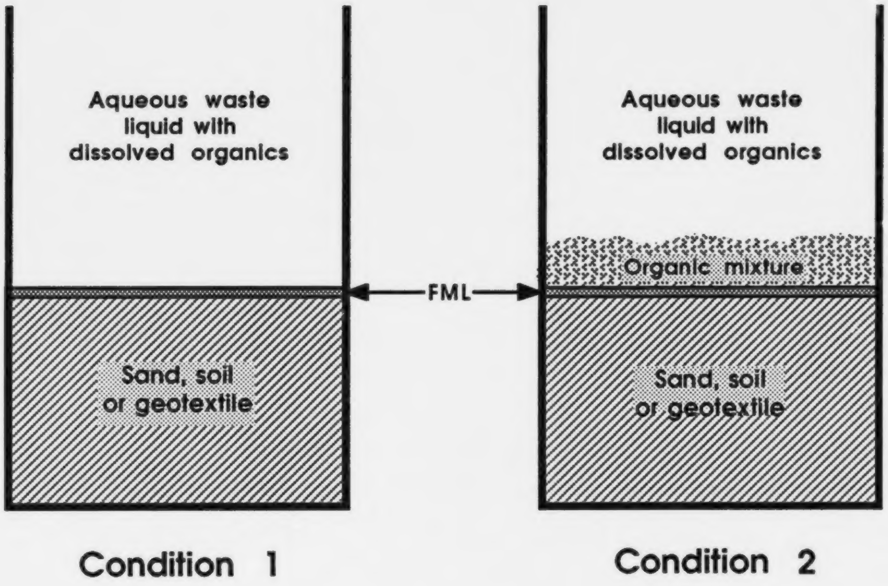
Aqueous waste liquid with dissolved organics
Aqueous waste liquid with dissolved organics
Organic mixture
FML
Sand, soil or geotextile
Sand, soil or geotextile
Condition 1
Condition 2

Figure 1. Two conditions that FMLs could encounter when in contact with waste liquids in waste storage and disposal facilities.

In the first condition, the waste liquid that contacts the liner consists of water with dissolved organics and probably some inorganics. Though inorganics in a waste liquid may affect organic solubility, it is the organic constituents of the waste liquid that are of principal importance as they are potentially soluble in the FML. The ultimate absorption of an organic by the FML is determined by the relative solubility characteristics of the organics and the FML. Once the organic, either volatile or nonvolatile, has dissolved in the FML it will diffuse into, swell, and potentially permeate the FML. If the organic is volatile, it can evaporate into the pores of the soil on the downstream side. If it is water soluble, it could dissolve in water (such as condensation) on the downstream side, and migrate through the soil in the water.

In the second condition, the FML would be in direct contact with organic mixtures. Such a condition has been encountered in the field when organic concentrations, having a higher specific gravity than the waste liquid, exceed their solubility limit in water and collect on the FML. In this case, the layer would consist of a mixture of several organics which can partition into the FML. The concentration of organics in the waste liquid directly in contact with the FML is considerably higher in the second condition and, consequently, the degree of swelling can be higher and subsequent transmission could be greater.

This project primarily addressed the subject of the solubility of organics in FMLs as determined by their relative solubility parameters and by other factors, such as the levels of crystallinity and crosslink densities of these FMLs. The subject of dilute solutions of organics and partitioning was also investigated in the study reported in Section 5 of dilute solutions of organics in water and in mixtures of organics.

SWELLING OF A POLYMERIC FML ON EXPOSURE TO WASTE LIQUIDS

Though most FMLs absorb constituents of the waste liquids and swell during exposure to liquids containing organics, highly plasticized membrane compositions, such as polyvinyl chloride (PVC) FMLs, can lose plasticizer and shrink. These two processes can take place simultaneously so that, in the case of plasticized compositions, the plasticizer can be extracted and, simultaneously, the organic constituents in a waste liquid can be absorbed and result in either a net swelling or loss.

Compatibility testing of an FML for waste storage and disposal facilities, such as is performed in EPA Method 9090 (EPA, 1984 and 1986), has been principally concerned with the effect on the physical properties of FMLs after immersion in the waste liquid or leachate that is to be contained. Absorption of the water and organics in the waste liquid and the resultant swelling of the FML can cause deterioration of many of the properties of the FMLs. This is the likely occurrence in the loss of properties; however, physical properties of FMLs other than tensile strength, elongation at break, tear resistance, puncture resistance, and gain in permeability can be affected by organics and waste liquids without showing much swelling. Of particular importance are the effects on semicrystalline FMLs which can, under simultaneous exposure to waste liquids and mechanical stress, be subject to environmental stress-cracking (ESC) and rupture.

The major factors involved in the magnitude of swelling of polymeric compositions in a liquid are:

- Solubility parameter value of the polymer with respect to that of constituents of the liquid.
- Crosslinking of the polymer.
- Crystallinity of the polymer.
- Filler content of the compound.
- Plasticizer content of the compound.
- Soluble constituents in the compound.

Due to differences in polymers and in compounding, some of these factors do not apply or become important.

For rubber and noncrystalline or amorphous polymers, the solubility parameter is probably the most important factor in swelling and, as noted above, is used by polymer scientists to measure the compatibility of an amorphous polymeric composition with a liquid with which it may be in contact.

Crosslinking of a noncrystalline polymer or a rubber reduces its ability to swell in a liquid which has similar solubility characteristics to the polymer. The amount of swelling of a crosslinked polymer in a good solvent for the raw polymer can be used as a measure of the degree of crosslinking: the greater the crosslinking, the less the swelling.

Crystallinity of a polymer acts much like crosslinking to reduce the ability of a polymer to dissolve. The crystalline domains of a polymer do not absorb organics. Highly crystalline polymers, such as HDPE, will swell slightly but will not dissolve in gasoline even though they are both hydrocarbons.

Two additional factors in FML compositions that also can affect the magnitude of swelling of noncrystalline polymers are the amount of filler used in the recipe, e.g. carbon black, silica, or clay, and the amount of plasticizer. As with the crystalline domains in semicrystalline polymers, fillers do not absorb organics. Generally, in the latter case the plasticizer is extractable by organic solvents, but only slightly extractable by water.

Rubber and plastic compounds may contain minor amounts of water soluble inorganic salts which enter the compound via the polymer itself, e.g. catalyst traces, salt used in flocculation, etc., and via small amounts in the various compounding ingredients, e.g. many of the non-black fillers contain small amounts of water-soluble constituents. These water-soluble salts can cause swelling by diffusion of water into the mass by the driving force of osmosis.

SOLUBILITY PARAMETERS

Solubility parameters have found wide use in determining the solubility of polymeric materials in various organics. Some of the many applications are reviewed by Barton (1975), such as in the paint and coatings industry. Also of particular interest are the uses of this parameter in studying the plasticization of polymers, in preparing rubber blends, and in designing rubber and plastic compositions for contact with various oils, hydraulic fluids, and gasoline (Beerbower et al, 1963 and 1967). The latter application is similar to that used in assessing the swelling and performance characteristics of FMLs that might be exposed to waste liquids containing organics.

The solubility parameter (δ) and cohesive energy density (CED) are concepts related by the following equation (Hildebrand and Scott, 1950, p 56):

$$\delta = (\mathrm{CED})^{1/2} = (\Delta E/V_m)^{1/2} \qquad (1)$$

where

ΔE = the energy required to vaporize one mole of material

V_m = the molar volume.

Thus, δ is a measure of the potential energy of any material with respect to its energy in an entirely disassociated form and is free of any intermolecular interactions. Intuitively, two different organics of exactly equal potential energies should be mutually miscible in all proportions with no loss or gain of energy. This model of solubility, termed the solubility parameter model, was developed by Hildebrand (Hildebrand and Scott, 1950, p 119) and may be expressed by the equation:

$$\Delta E_{mix} = X_1 \, X_2 \, (\delta_1 - \delta_2)^2 \qquad (2)$$

where

ΔE_{mix} = the energy of mixing

$X_{1,2}$ = the volume fractions of components 1 and 2

$\delta_{1,2}$ = the solubility parameters of components 1 and 2.

Clearly, the mathematical model agrees with intuition in concluding that equal solubility parameters imply no energy change on mixing.

The potential energy of organics may be simply expressed as δ, but is in fact a sum of energies due to several different types of molecular interaction. These include dipole-dipole interactions, London dispersion forces, hydrogen-bonding effects, and at very close distances, repulsive effects. These energies are approximately additive [Hildebrand and Scott, 1950 (p 56); Gardon and Teas, 1976 (p 428); Hansen, 1967 (p 104)]:

$$E_{total} = E_1 + E_2 + E_2 + \ldots \qquad (3)$$

It follows from equation (1) that:

$$\delta^2_{total} = \delta^2_1 + \delta^2_2 + \delta^2_3 + \ldots \qquad (4)$$

Consideration of the individual contributions of the solubility parameter components becomes quite important in determining the solubility of complex systems such as polymers. These do not behave in the "ideal" manner assumed in construction of the solubility parameter model and consequently solubility is sensitive to variations in the component solubility parameters, not just the overall solubility parameters.

In order to properly describe the solubility of polymers, models more complex than Hildebrand's solubility parameter model are required. The most important model of this general form was proposed by Hansen (1967) and is termed the three-dimensional solubility parameter model. It is written as:

$$\delta^2_{total} = \delta^2_d + \delta^2_p + \delta^2_h \qquad (5)$$

where

δ_{total} = total Hansen solubility parameter

δ_d = the contribution to the total solubility parameter due to intermolecular London dispersion forces

δ_p = the contribution due to intermolecular dipole interactions

δ_h = the contribution due to intermolecular hydrogen-bonding.

Approaches taken by various researchers are described in Beerbower et al (1963), Gardon and Teas (1976), and Van Krevelen and Hoftyzer (1976). A generally useful model will probably require parameters defining polymer crosslinking and crystallinity as well as polymer solubility parameters, and may well not be amenable to a simple graphic presentation.

Comprehensive tabulations of solubility parameters for common solvents and other organic chemicals have been made by Barton (1975 and 1983). Many more data are available in other references, and discrepancies exist among the data for a given organic. Typical solubility parameter values for some common organics of different chemical types are presented in Table 1.

TYPE AND COMPOSITION OF POLYMERIC FMLS

Polymers used in the manufacture of FMLs include rubbers and plastics differing in basic chemical composition and structure, solubility characteristics, chemical resistance, and the mode in which they deteriorate and ultimately fail. These polymers can be classified into four general types:

- Rubbers (elastomers) that are generally crosslinked.
- Thermoplastic elastomers that are not crosslinked.
- Thermoplastics that are generally not crosslinked.
- Thermoplastics that have a relatively high crystalline content, such as the polyethylenes.

Table 2 lists the types of polymers that are used in the manufacture of FMLs and shows the abbreviations used in this report. The polymers most frequently used in liners have been PVC, chlorosulfonated polyethylene (CSPE), chlorinated polyethylene (CPE), butyl rubber (IIR), ethylene propylene rubber (EPDM), neoprene (CR), and HDPE. The thickness of commercial FMLs ranges from 0.5 to 3.0 mm (20-120 mil), with most in the 0.75 to 1.5 mm (30-60 mil) range.

Most FMLs are based on single polymers, but compounds based on blends of two or more polymers are being developed and used in FMLs. Also, different grades (varying in molecular weight, branching, or crosslinking) of a given type of polymer may be used. Such variations can affect the solubility characteristics of the FML. Generic classifications based on individual polymers have become increasingly difficult, even though one polymer may predominate. All polymers are compounded with auxiliary ingredients which serve different purposes and may also significantly affect solubility characteristics as well as permeability and other physical properties.

Several of the components of a liner formulation can be affected during service when the liner is either immersed in the liquid or exposed to the weather. Low molecular weight fractions in the original polymer or blend can be lost. The oils and plasticizers are potentially extractable and, in some cases, biodegradable; antidegradants can be consumed and can be extracted. Loss or change in any of these components can affect properties and, thus, compatibility or durability of the compound.

Most of the FMLs currently manufactured are thermoplastic or semicrystalline. Even if the polymer in the crosslinked form is more chemically resistant (such as CPE and CSPE), it is generally supplied as a

TABLE 1. SOLUBILITY PARAMETER VALUES[a] FOR SELECTED SOLVENTS

Name	δ, $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$				
	δ	δ_t	δ_d	δ_p	δ_h
Alkanes					
n-Octane	7.6	7.6	7.6	0.0	0.0
Cyclohexane	8.2	8.2	8.2	0.0	0.1
Aromatic hydrocarbons					
Toluene	8.9	8.9	8.8	0.7	1.0
o-Xylene	8.8	8.8	8.7	0.5	1.5
Tetrahydronaphthalene	9.5	9.8	9.6	1.0	1.4
Halohydrocarbons					
1,1-Dichloroethylene	9.1	9.2	8.3	3.3	2.2
Ethylene dichloride	9.8	10.2	9.3	3.6	2.0
Carbon tetrachloride	8.6	8.7	8.7	0.0	0.3
Tetrachloroethylene	9.3	9.9	9.3	3.2	1.4
1,1,2,2-Tetrachloroethane	9.7	10.6	9.2	2.5	4.6
Ethers					
Epichlorohydrin	11.0	10.7	9.3	5.0	1.8
Tetrahydrofuran	9.1	9.5	8.2	2.8	3.9
Ketones					
Acetone	9.9	9.8	7.6	5.1	3.4
Methyl ethyl ketone	9.3	9.3	7.8	4.4	2.5
Diethyl ketone	8.8	8.9	7.7	3.7	2.3
Aldehydes					
Furfural	11.2	11.9	9.1	7.3	2.5
Esters					
Ethyl acetate	9.1	8.9	7.7	2.6	3.5
Di-n-butyl phthalate	9.3	9.9	8.7	4.2	2.0
Tributyl phosphate	8.8	8.9	8.0	3.1	2.1
Tricresyl phosphate	8.4	11.3	9.3	6.0	2.2
Dioctyl phthalate	7.9	8.9	8.1	3.4	1.5
Nitrogen compounds					
Pyridine	10.7	10.7	9.3	4.3	2.9
Quinoline	10.8	10.8	9.5	3.4	3.7
Formamide	19.2	17.9	8.4	12.8	9.3
Dimethyl formamide	12.1	12.1	8.5	6.7	5.5
Sulfur compound					
Carbon disulfide	10.0	9.9	5.3	8.1	2.1
Monohydric alcohol					
Ethanol	12.7	13.0	7.7	4.3	9.5
1-Propanol	11.9	12.0	7.8	3.3	8.5
1-Octanol	10.3	10.3	8.3	1.6	5.8
Carboxylic acid					
Acetic acid	10.1	10.5	7.1	3.9	6.6
Phenol					
m-Cresol	10.2	11.1	8.8	2.5	6.3
Polyhydric alcohol					
Ethylene glycol	14.6	16.1	8.3	5.4	12.7
Water	23.4	23.4	7.6	7.8	20.7

[a] 25°C solubility parameters: δ = Hildebrand parameter; Hansen parameters: δ_t = total; δ_d = dispersive; δ_p = polar; δ_h = hydrogen-bonding. Metric unit $\mathrm{MPa}^{1/2} = 2.045 \times \mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$.

Source: Barton (1975).

thermoplastic because it is easier to make reliable seams and repairs in the field. FMLs based on thermoplastic polymers can be heat-sealed or seamed with a solvent or bodied solvent. Semicrystalline FMLs which are also thermoplastic are generally seamed by various thermal welding or fusion methods.

TABLE 2. POLYMERIC MATERIALS USED IN LINERS

Polymer	Abbreviation	Type of compound[a]	Thickness, mm	Fabric reinforced
Butyl rubber	IIR	XL	0.9-2.3	Yes, no
Chlorinated polyethylene	CPE	TP	0.5-1.0	Yes, no
Chlorosulfonated polyethylene	CSPE	TP,XL	0.6-1.0	Yes, no
Elasticized polyolefin	ELPO	CX	0.6	No
Elasticized polyvinyl chloride	PVC-E	TP	0.8-0.9	Yes
Epichlorohydrin rubber	ECO	XL	1.67	Yes, no
Ethylene propylene rubber	EPDM	XL,TP	0.5-1.6	Yes, no
Neoprene	CR	XL	0.5-1.8	Yes, no
Nitrile rubber	NBR	XL	0.8	Yes
Polyester elastomer	PEL	CX	0.18	No
Polyethylene:				
Low density	LDPE	CX	0.3-0.8	No
Linear low-density	LLDPE	CX	0.5-0.8	No
High density	HDPE	CX	0.5-3.1	No
High-density alloy	HDPE-A	CX	0.3-1.0	No
Polyvinyl chloride	PVC	TP	0.3-0.9	Yes, no
Polyvinyl chloride, oil resistant	PVC-OR	TP	0.8	Yes, no

[a] TP = thermoplastic; CX = semicrystalline; XL = crosslinked.

The solubility parameter of a polymer is generally measured by immersing specimens in organics of different solubility parameter values and observing the swelling or the dissolution of the polymer when the parameters of the two approach equality, as illustrated in Figure 2. Table 3 presents polymer solubility parameter data that were obtained in this manner on pure or slightly crosslinked polymers, most of which are or have been, used in the manufacture of FMLs.

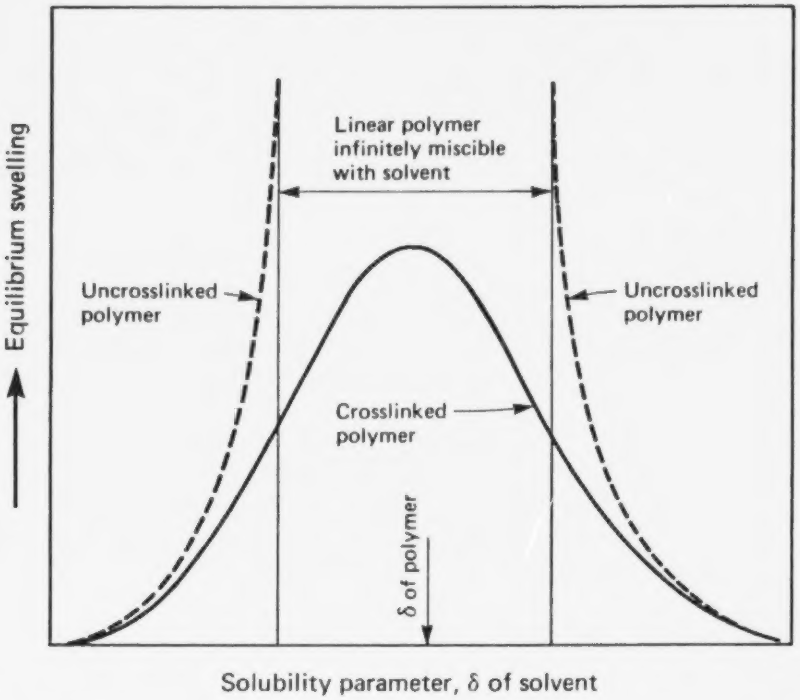

Figure 2. Equilibrium swelling as a function of the solubility parameter of the organic for an uncrosslinked and crosslinked polymer (Van Krevelen and Hoftyzer, 1976).

COMPARISON OF THE SOLUBILITY PARAMETERS OF COMMON SOLVENTS AND POLYMERS

Figure 3 shows the solubility parameters of common solvents and some of the polymers that are used or potentially useful in the manufacture of lining materials. A distribution of the solubility parameters of solvents is also shown by the type of solvent. These data show that a high proportion of the common organics and polymers fall within a solubility parameter range of 8 to 10; they thus indicate that a large degree of swelling might take place when polymers are in contact with waste liquids that contain these solvents and possibly dissolution of the polymer will occur.

SWELLING OF MEMBRANES BASED ON DIFFERENT POLYMERS IN A DILUTE AQUEOUS SOLUTION OF AN ORGANIC CHEMICAL

As indicated above, the most probable liquid that liners will encounter is a dilute aqueous solution in which organics are dissolved constituents. In this case, the organic chemicals that are solutes in the water will partition with the polymeric membrane. This condition is similar to that encountered in the bioconcentration of nondegradable toxic organics dissolved in water that enter the biota and the food chain. In that case, water-octanol partitioning coefficients have become very useful in predicting the tendency of particular organics toward bioconcentration (Leo et al, 1971).

TABLE 3. HILDEBRAND SOLUBILITY PARAMETERS[a] OF DIFFERENT POLYMERS[b]

Polymer	Average	Range	Number of determinations
Butadiene/acrylonitrile, 75/25	9.38	9.25-9.50	4
Butyl rubber	7.84	7.70-8.05	5
Ethylene propylene rubber	7.95	7.90-8.00	2
Neoprene	8.85	8.18-9.38	4
Polyethylene	7.94	7.87-8.10	4
Polytetrafluoroethylene	6.2	...	1
Polypropylene	8.1	...	1
Polyvinyl chloride	9.57	9.48-9.70	3
Chlorinated rubber[c]	9.55	8.5-10.6	...
Chlorosulfonated polyethylene[c]	8.55	8.1-9.6	...
Polyvinylidene chloride	12.4	12.2-12.6	2
Silicone rubber	7.4	7.3-7.55[d]	2

[a] $cal^{1/2}\ cm^{-3/2}$.

[b] Source - Sheehan and Bisio (1966).

[c] Source - Burrell (1966).

[d] Source - Hauser et al (1956).

These coefficients were explored as they might be applied to dissolved organic waste constituents and polymeric FMLs. Partitioning coefficients for dissolved organics between water and polymeric membrane materials were not located in the literature. Matrecon made an initial study (Haxo et al, 1985a) of immersing a variety of lining materials in a dilute saturated solution of tributyl phosphate (TBP). This organic has reported solubility parameters ranging from 8.5 to 9.0 and a solubility in water of less than 0.1%. Selected data from this study are presented in Table 4. The data show that, on long exposures, though the concentration of TBP in the water is low, the absorption of TBP and possibly some water by the membranes can reach significant values in which the properties are greatly deteriorated. The data also show that polymers that have solubility parameters differing from the TBP swell less than those that have solubility parameters in the range of 8.5 to 9.0. Also, the CPE that was crosslinked swelled much less than the thermoplastic CPE. Those membranes that were semicrystalline swelled the least. Such results indicate that factors in addition to solubility parameters must be considered in estimating swelling and ultimately estimating service life.

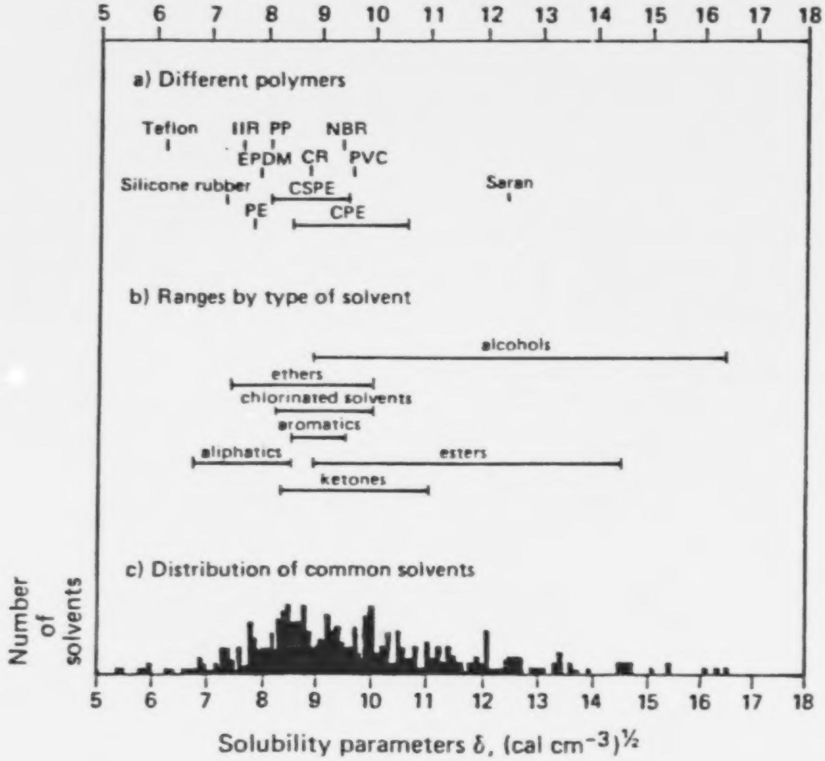

Figure 3. Solubility parameters of common solvents and polymers (data from Barton, 1975, and Burrell, 1970).

TABLE 4. EFFECTS ON PROPERTIES OF MEMBRANES[a] ON IMMERSION IN A DILUTE[b] AQUEOUS SOLUTION OF TRIBUTYL PHOSPHATE FOR 522 DAYS

Polymer	Butyl	CPE	CPE	CSPE	ELPO[c]	EPDM	Neoprene	PEL[d]	PVC	HDPE	LDPE	PP
Type of compound	XL	TP	XL	TP	TP	XL	XL	TP	TP	CX	CX	CX
Matrecon number	44	77	100	55	36	91	90	75	59	105	108	106
Initial thickness, mil	63	30	36	33	23	32	35	7	33	32	31	33
Analytical properties:												
Weight gain, %	21.9	107.2	34.4	31.6	6.7	5.2	41.4	4.5	46.2	0.56	0.51	0.18
Extractables, original, %	11.8	9.1	17.4	4.1	5.5	23.6	21.5	2.7	35.9	...	2.1	...
Gain in volatiles[e], %	2.2	42.2	19.7	20.7	2.1	4.3	24.8	4.1	11.9	0	0	0
Physical properties[f]:												
Final thickness, mil	64.3	47.9	40.9	37.9	20.2	36.8	43.5	6.6	36.4	31.5	30.9	32.2
Tensile strength, % retention	107	10	63	48	48	93	49	89	31	88	104	97
Elongation at break, % retention	115	155	79	79	74	106	82	101	89	101	102	105
Stress at 100% elongation, % retention	74	6	46	80	70	81	15	90	28	92	103	110
Tear resistance, % retention	...	14	29	39	79	105	34	90	23	81	86	91
Hardness change, points	-2	-60	-20	-14	-3	-1	-25	-109[g]	-33	-1	-20	-2
Puncture test:												
Stress, % retention	73	20	85	112	101	107	66	77	48	101	92	94
Elongation, % retention	126	127	125	131	142	111	119	100	133	107	108	42

[a] All materials are unreinforced.

[b] A saturated solution of tributyl phosphate in deionized water, ca. 1000 mg/L.

[c] Elasticized polyolefin.

[d] PEL = Polyester elastomer.

[e] Mostly water that had been absorbed.

[f] Data for tensile, elongation, stress at 100% elongation (S-100), and tear are the averages of measurements made in both machine and transverse directions.

[g] Due to curling of sample, magnitude of change as reported is probably too great.

Source: Haxo et al (1985).

SECTION 5

SWELLING OF FMLS IN NEAT ORGANICS AND DETERMINATION OF SOLUBILITY PARAMETERS OF FMLS

INTRODUCTION

This section describes the experimental methods and presents the results of the study to determine the solubility parameters of (1) polymers used in the manufacture of FMLs and of (2) actual commercial FMLs used in water and waste containment and control. These parameters were determined by measuring the equilibrium volume swelling of 28 polymeric materials after immersion in 30 different neat organics of known solubility parameters and in water. These test liquids were selected so that those included in the study represented a wide range of solubility parameters. The equilibrium swelling data were plotted for each polymeric composition as a function of each of the four solubility parameters of the organics in which the compositions had been immersed. These parameters included the Hildebrand parameter (δ_o) and the three component parameters, i.e. the dispersive (δ_d), the polarity (δ_p), and the hydrogen-bonding (δ_h) parameters. The equilibrium swelling values for each of 28 polymeric compositions in each of 31 test liquids are presented.

The method by which a computer generated the four solubility parameters from the swelling data for each of the polymeric compositions is described and the results are presented.

DESIGN OF THE EXPERIMENT

FMLs are made from a variety of different polymers. The composition of an FML may be based on either a single polymer or mixtures of polymers and may also include additives such as fillers, plasticizers, and antidegradants, many of which could affect the level of absorption of constituents of the waste liquid with which it may be in contact (Matrecon, 1983). The general compositions of the polymeric compounds in various types of FMLs are presented in Table 5. Crosslinking of the polymeric component of an FML compound by the addition of curatives or by internal reaction within the polymer tends to reduce swelling. FMLs compounded with monomeric plasticizers can be extracted by the waste liquid; in this case the FML may then shrink and become stiff. Crystallinity in a composition such as polyethylene reduces absorption and swelling depending upon the percent of the crystalline phase in the composition. Swelling occurs only in the amorphous phase, i.e. the noncrystalline phase. These factors complicate the determination of the solubility parameters by affecting the magnitude of swelling of the FML, but they should not affect the values of the solubility parameters. Several simple and slightly crosslinked compounds of single polymers, which would swell but would not dissolve, were prepared and included in the immersion studies.

TABLE 5. BASIC COMPOSITIONS OF POLYMERIC FML COMPOUNDS

	Composition of compound type, parts by weight		
Component	Crosslinked	Thermoplastic	Semi-crystalline
Polymer or alloy	100	100	100
Oil or plasticizer	5-40	5-55	0-10
Fillers:			
Carbon black	5-40	5-40	2-5
Inorganics	5-40	5-40	...
Antidegradants	1-2	1-2	<1
Crosslinking system:			
Inorganic	5-9	[a]	...
Sulfur	5-9	...	...

[a] An inorganic curing system that crosslinks over time is incorporated in CSPE FML compounds.

In order to cover the range of possible component solubility parameters of the polymers used in the manufacture of liners, particular attention was paid to the selection of the organics in order to cover a broad range of component solubility parameters that might exist in the polymers. The selection of the organics, the FMLs, and the preparation of the simple polymeric compounds are described in the following sections.

SELECTION OF TEST ORGANICS

The first task in selecting the organics to be used in this study was to choose a group of organics that met the following basic requirements:

- The full range of values of the different component solubility parameters should be covered.
- Known common organic constituents found in waste streams should be included.
- Organics known to be in the wastes that were tested in our previous work should be included.

Other factors considered were the following:

- Solubility of the organic in water.
- Density, melting point, and boiling point of the organic.
- Vapor pressure of the organic.
- Toxicity and safety aspects of the organic.

The most difficult criterion to satisfy was to cover the full range of all four solubility parameters.

Choosing organics based upon information on component solubility parameters was more complex than making the choice on the basis of the Hildebrand parameter alone. By selecting organics representing the full range of each of the component parameters, interactions between the three parameters could be analyzed. The selection of the organics was made by using a computer to classify them with respect to the magnitude of the individual component solubility parameters and then to apply the other criteria to make the final selection.

The classification procedure was as follows: the 131 organics in the database from Barton (1975) were listed in order of increasing δ_d value. Those in the lowest third of the list were coded with a 1, those in the middle third with a 2, and those in the highest third with a 3. This process was repeated for the organic δ_p and δ_h values with the result that each organic was assigned a three-digit code. Table 6 presents the ranges for

TABLE 6. CODING OF ORGANICS AND RANGES OF COMPONENT SOLUBILITY PARAMETER VALUES[a]

Level of values	Range value assigned to organic	Component solubility parameter[b]		
		(δ_d)	(δ_p)	(δ_h)
Low values	1	6.0-7.8	0-2.5	0-2.2
Medium values	2	7.9-8.7	2.6-4.2	2.3-5.0
High values	3	8.8-10.0	4.3-12.8	5.2-20.7

[a] Based on ordering of organics in the data based from Barton (1975) by individual solubility parameter.

[b] δ_d = dispersive component; δ_p = polarity component; and δ_h = hydrogen-bonding component.

coding the organics by component parameter values. Each code labeled a group of organics which had values in the same range for each of the component parameters. A single organic which best met the remaining organic criteria was then chosen from each of the 27 possible groups. This procedure resulted in a base list of 27 organics. This list was supplemented with three additional organics and water, each of which is unique or of special interest. The additional organics were isooctane, a mixture of m-, o-, and p-xylenes, and acetone. Table 7 lists all of the selected organics by class. Appendix A lists the organics and water by the assigned three-digit code and presents selected data on each.

TABLE 7. ORGANICS USED IN THE SWELLING EXPERIMENTS BY TYPE OR CLASS

Class of organic	Specific organic
Alkanes	n-Octane Isooctane Cyclohexane
Aromatic hydrocarbons	Xylenes (mixture of o-, m-, and p-) Tetrahydronaphthalene "Tetralin®"
Alcohols	Methanol 2-Ethyl-1-hexanol n-Propanol Cyclohexanol Benzyl alcohol Furfuryl alcohol Ethylene glycol
Chlorinated hydrocarbons	Tetrachloroethylene Trichloroethylene
Esters	Di(ethylhexyl) phthalate Diethyl phthalate Isoamyl acetate Ethyl acetate Diethyl carbonate Butyrolactone Propylene carbonate
Ketones	Acetone Methyl ethyl ketone Cyclohexanone Methyl isobutyl ketone
Nitrogen compounds	Nitroethane N,N-Dimethylacetamide Quinoline 2-Pyrrolidone
Phenols	m-Cresol

SELECTION OF FMLS AND OTHER COMPOSITIONS

Twenty-eight different polymeric compositions, including 22 commercial products which represented a wide range of compositions that have been or are being used as FMLs, and six laboratory prepared compositions were selected for testing in this experimental study. The following criteria were used in selecting FMLs for immersion testing with the various organics:

- The final selection should represent a range of different polymers used in the manufacture of FMLs for lining waste and disposal facilities.
- Inasmuch as FMLs are based on thermoplastic, amorphous, and semicrystalline polymers, compositions based on all these types should be included in the final selection. The semicrystalline polymers should contain both amorphous or rubber-like phases, which can absorb organics, and crystalline phases, which do not absorb organics.
- Amorphous crosslinked materials, e.g. elastomers, should be included to assess the effect of crosslinking.
- Several compositions should be represented within a type of polymer to assess compounding variations. One way to fulfill this requirement would be to select FMLs of the same polymer type but produced by different manufacturers.
- Polyethylenes of different crystallinity and type should be included, i.e. ranging from low density to high density.
- Polyethylene alloyed with an elastomer to reduce environmental stress-cracking should be included.
- FMLs previously tested by Matrecon should be included.
- Simple polymeric compositions of known composition should be included. They should contain a minimum number and amount of compounding ingredients and should be only lightly crosslinked. Such compositions are useful for determining the solubility parameters of polymers because they reduce the effects of compounding ingredients on the absorption of organics. Also, if sufficiently crosslinked, they will swell without dissolving in any of the organics that do not chemically react with them.

All of the polymeric compositions selected for the swelling tests are listed in Table 8, which includes data on their respective extractables contents and specific gravities. Additional analytical and physical property data on each material are presented in Appendix B. Of the commercial materials 11 were based on relatively simple compositions. They include an ethylene vinyl acetate (EVA) FML, two polyester elastomer (PEL) sheetings, a developmental polybutylene (PB) FML, six polyethylene FMLs, and one polyurethane (PU)

TABLE 8. POLYMERIC COMPOSITIONS IN SWELLING TEST

Polymer	Matrecon identification number	Type of polymer[a]	Property		
			Extractables, %	Extraction organic[b]	Specific gravity
Chlorinated polyethylene	195	TP/AM	14.85	n-heptane	1.260
	335R	TP/AM	4.48	n-heptane	1.313
	378R	TP/AM	7.94	n-heptane	1.333
Chlorosulfonated polyethylene	169R	TP/AM	11.29	acetone	1.297
	174R	TP/AM	7.15	acetone	1.364
	DOY-3[c]	TP/AM	<1.0[d]	...	1.147
	DOZ-2[c]	TP/AM	<1.0[d]	...	1.401
	DPO[c]	TP/AM	<1.0[d]	...	1.193
	DPP[c]	TP/AM	<1.0[d]	...	1.143
Epichlorohydrin rubber	178	XL/AM	7.63	MEK	1.458
Ethylene propylene rubber	232	XL/AM	22.78	MEK	1.166
Ethylene vinyl acetate	308A	TP/AM	0.75	ethanol	0.951
Neoprene	168	XL/AM	11.23	acetone	1.500
Nitrile rubber	DPN[c]	XL/AM	<1.0[d]	...	1.024
Polyester elastomer	316	TP/CX/AM	1.09	n-heptane	1.149
	323	TP/CX/AM	≤ 0.6	n-heptane	1.253
Polybutylene	221A	CX	3.68	MEK	0.907
Polyethylene:					
Low-density	309A	CX	1.85	MEK	0.938
Linear low-density	284	CX	0.65	MEK	0.929
High-density	184	CX	0.73	MEK	0.951
	263	CX	≤ 0.6	MEK	0.953
	305	CX	0.98	MEK	0.954
HDPE/EPDM-alloy	181	CX	2.09	MEK	0.949
Polyurethane	351	TP/AM	1.50	n-heptane	1.118
Polyvinyl chloride	153	TP/AM	34.57	2:1 CCl_4:CH_3OH[e]	1.263
	DPQ[c]	TP/AM	40.12	2:1 CCl_4:CH_3OH[e]	1.226
Elasticized polyvinyl chloride	176R	TP/AM	9.13	CH_3OH	1.219
Polyvinyl chloride, oil resistant	144	TP/AM	30.97	2:1 CCl_4:CH_3OH[e]	1.356

[a] TP = thermoplastic; AM = amorphous; XL = crosslinked; CX = semicrystalline; R = fabric reinforced.

[b] MEK = Methyl ethyl ketone.

[c] Laboratory-prepared compound, the composition of which is presented in Appendix B.

[d] Calculated from compound formulation.

[e] By volume.

sheeting. The remaining commercial compositions are all FMLs, the compositions of which are not precisely known. Included are three CPEs, two CSPEs, one epichlorohydrin rubber (ECO), one EPDM, one CR, and three different PVCs. The laboratory-prepared compounds included four CSPE compositions, a nitrile rubber (NBR) composition, and a PVC composition plasticized with di(ethylhexyl) phthalate. Among the four CSPE compositions are three "gum" compounds (i.e. compounds that contain no filler) which vary in the level of crosslinking. The fourth CSPE composition, which contains 100 parts of carbon black, is similar to that used in CSPE FML compounds. These laboratory-prepared compounds of known polymer content and composition should furnish more precise information as to the solubility parameter values of the individual polymers. As discussed below, these are the types of compositions normally used to measure the solubility parameters of polymers. The data that are obtained with laboratory-prepared compositions are compared with the solubility parameters obtained with FMLs containing the same type of polymers.

TEST PROCEDURE

To determine the equilibrium swelling of each polymeric material, the volume of an immersed sample was monitored by weight change until a maximum value (i.e. equilibrium) was reached. A sample consisted of three FML specimens, which were placed in a 20 mL disposable scintillation vial for each combination. The inside of the vial cap was lined with Teflon-coated aluminum foil to prevent the loss of organics. The 20 mL vial was satisfactory for most combinations of polymeric compositions and organics; however, for those combinations in which excessive swelling took place, the specimens were transferred to 70 mL vials. In all vials, the specimens were hung so they did not touch each other.

The specimens, which measured 0.5 x 1.5 in., were cut from slabs or sheetings with a die used for cutting out ESC specimens (ASTM D1693). However, the specimens were treated as a unit, not individually, and were weighed as a set before and after immersion. This procedure allows more of a sample to be immersed in a small container and increases the sensitivity of the determination as it provides an averaging of data for three specimens. The drawback is the possibility of weighing errors, but this was not a significant problem as the test was not terminated until the weights on two consecutive weighings showed reasonable agreement. Before immersion, the weight of the sets of specimens ranged from 0.5 to 5 g with most weighing under 2 grams.

The specimens were weighed before immersion and after 2 days, 1 week, and 2 weeks. Additional weighings were taken approximately once a week if the specimens had not reached equilibrium after the second week of exposure. Once equilibrium swelling had been reached, the equilibrium swelling based on volume was calculated from the equilibrium swelling based on change in weight. The volume increase was calculated by correcting for the density of the respective organics used to swell the FML specimens.

RESULTS OF THE SWELLING TEST

The final data for the equilibrium swelling of the 28 FMLs and laboratory-prepared polymeric compositions in each of the 30 organics and in water are presented in Appendix C. The data for each composition are presented in increasing order of the Hildebrand solubility parameter of the organic. The swelling data ranged from values that were a minor fraction of a percent to complete dissolution and disintegration. Generally, for a given FML the swelling as a function of a solubility parameter went through dissolution or a maximum swell with increasing values of the Hildebrand solubility parameter. The maximum is an indication of the solubility parameter of the specific polymeric composition.

Those compositions that swelled more than 1000%, dissolved, or disintegrated are designated by "D" in the Appendix C. Some of those materials that had high levels of plasticizers initially lost weight but later swelled.

DISCUSSION OF THE SWELLING DATA

Considerable variation in the volume changes can be observed among the polymeric materials in the different organics. It should also be noted that the magnitude of swelling in many organics does not follow the Hildebrand solubility parameter. This shows the need to consider other parameters and other factors in predicting the swelling of FMLs in liquids that contain organics.

The swelling data relating to each of the broad types of polymeric materials are discussed by type in the following subsections, followed by some general comments.

Chlorinated Polyethylene

Three CPE FMLs (Liners Nos. 195, 335R, and 378R) were included in this swelling study, one of which was unreinforced. The three contained different amounts of plasticizer, as shown by their respective extractables contents (Appendix C). The responses of the three CPEs to the different organics varied. The greatest swelling was in the organics with Hildebrand solubility parameters in the range of 8.3 to 11.1 $cal^{1/2}\ cm^{-3/2}$. All of the CPEs were decomposed by the Tetralin and quinoline. Two of the three were dissolved or disintegrated by methyl isobutyl ketone, isoamyl acetate, and trichloroethylene. As the CPE FMLs did not respond in the same way to all of the organics, they may have been based on different polymers as well as having different plasticizer contents. If so, they may have different solubility parameters. The CPEs were thermoplastic, as shown by their high swelling and dissolution in some of the organics.

Chlorsulfonated polyethylene

Six CSPE compositions were included in this swelling study. Two were commercial FMLs; one (Liner No. 169R) was a potable grade and the other (Liner No. 174R) was an industrial grade. Overall, the industrial grade swelled less in most of the organics and in water. However, immersion in some organics resulted in the opposite. For example, the trichloroethylene dissolved the industrial-grade CSPE, but did not dissolve the potable grade. The greatest swelling took place in the organics with Hildebrand solubility parameter values in the range of 8.2 to 10.8 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$.

The remaining four CSPE compositions were prepared in the laboratory. They were based on the one grade of CSPE polymer that is used in the manufacture of CSPE FMLs, but were compounded to maximize swelling without dissolving and to study different cure systems. Two compositions were prepared with different levels of peroxide curative to determine the effect of different levels of crosslinking (DPO and DPP). Both were compounded without filler. A third composition (DOY-3), also compounded without filler, had an MgO cure similar to the cure used in potable-grade CSPE FML compounds. The fourth also had an MgO cure and contained 37 volume percent of carbon black (DOZ-2). This last composition is similar to CSPE FML compositions. With the peroxide curing systems the number of crosslinks generally is proportional to the amount of peroxide added. The MgO cure, which is used in potable-grade CSPE FMLs, forms a different type of crosslink which develops with time with the absorption of moisture from the air or ground. Although the magnitude of swelling varied, the locations of the maximum swelling with respect to Hildebrand solubility parameter were the same as those of the commercial FMLs, i.e. in the range of 8.2 to 10.8 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$.

The results for the four laboratory-prepared CSPE compositions in the 30 organics and in water differ considerably in the magnitude of swelling. Swelling of the compound with the higher of the two peroxide contents is less in almost all of the organics, but it is not proportional to the peroxide content. The swelling of the unfilled compound with the MgO cure differs considerably from the swelling of the compounds cured with peroxide. The difference probably reflects the crosslinking with time that takes place with CSPE compositions containing MgO as the curative. The carbon black composition generally swells less than the corresponding MgO-cured compound, due to the lower CSPE content of the carbon black-filled compound. Immersion in those organics in which all of the CSPE compositions without filler swelled considerably resulted in specimens of the carbon-black-containing composition swelling excessively and disintegrating. The solubility parameters of these organics match relatively closely those of the CSPE, as is discussed in the subsection on the calculation of the solubility parameters from the swelling data.

Epichlorohydrin Rubber

One sample of a commercial-grade ECO FML (Liner No. 178) was included in this swelling study. None of the specimens of this FML disintegrated in any of the organics, as it was crosslinked. The greatest swelling values of this FML were after immersion in organics with Hildebrand solubility parameter values ranging from 9.6 to 12.9 $\mathrm{cal}^{1/2}\ \mathrm{cm}^{-3/2}$. The greatest swelling was in m-cresol. In the octanes the swelling was minimal, which reflects the high resistance which the ECO is expected to have to petroleum oils and fuels. The ECO, however, had the greatest swelling (23.6%) in water of all the polymeric compositions tested in this study.

Ethylene Propylene Rubber

The EPDM FML included in this swelling study was a crosslinked polymer. Overall, it showed low swelling, except in the aliphatics, aromatics, and chlorinated organics. The low swelling reflects the crosslinking and the fact that, at the start of the immersion, the composition contained considerable extender oil, which may have leached out. None of the specimens disintegrated. The greatest swelling took place in organics with Hildebrand solubility parameter values in the range of 7.0 to 9.9 $cal^{1/2}\ cm^{-3/2}$.

Ethylene Vinyl Acetate

A single sample of the EVA FML (Liner No. 308A) was included in this swelling study. Although it was a thermoplastic material, it did not disintegrate or dissolve completely in any of the organics. The greatest swelling took place in the organics with Hildebrand solubility parameter values in the range of 7.0 to 9.9 $cal^{1/2}\ cm^{-3/2}$. The chlorinated and aromatic organics caused the greatest swelling. The water absorption of the EVA FML at 0.66% was among the lowest of the materials in this study.

Neoprene

The CR compound used in this swelling study was a commercial FML (Liner No. 168) and was crosslinked. None of the specimens disintegrated, although they did show considerable swelling with the aromatics, the chlorinated organics, and cyclohexanone. The greatest swelling was in organics having solubility parameters in the range of 8.4 to 10.8 $cal^{1/2}\ cm^{-3/2}$. Among the organics with low solubility parameter values, e.g. the octanes, the CR had a low swelling which is consistent with its known oil resistance. Its swelling also was low in several other organics, such as some of the alcohols with higher solubility parameter values.

Nitrile Rubber

A laboratory-prepared NBR compound (DPN) was included in this swelling study. This rubber, which is recognized for its oil resistance, was compounded and cured without filler or plasticizer. It had a nitrile content of 33% and was lightly vulcanized and, consequently, it swelled considerably in organics in the middle range of the Hildebrand solubility parameter values, 9.3 to 11.1 $cal^{1/2}\ cm^{-3/2}$. One of the organics, m-cresol, caused disintegration.

Polyester Elastomer

Two samples of PEL were included in the swelling study, both of which were developmental materials and substantially different, as is shown in Table 9. In particular, the PEL Liner No. 316 had substantially lower crystallinity than PEL Liner No. 323, as is shown by lower heat of fusion and density. This difference in crystallinity is reflected by the substantially greater swelling of the PEL with the lower crystallinity. The greatest swelling of these FMLs was in those organics with Hildebrand solubility parameters in the range of 8.8 to 11.9 $cal^{1/2}$ $cm^{-3/2}$. The fact that both disintegrated in m-cresol indicates that both PELs tested in this study are thermoplastic materials. In the other organics, however, Liner No. 323 had a fraction of the swelling that occurred in Liner No. 316, showing the importance of crystallinity in polymeric materials of relatively similar composition.

TABLE 9. SELECTED DATA ON POLYESTER ELASTOMERS IN THE SWELLING STUDY

	Matrecon identification number	
Property	Liner No. 316	Liner No. 323
Melting point, °C	72	23
ΔH_f[a], cal/g	0.0157	0.567
Density at 23°C, g/mL	1.149	1.253

[a] Heat of fusion.

Polybutylene

A single sample of PB, which was a developmental FML (Liner No. 221A), was included in this swelling study. Its greatest swelling was in organics with Hildebrand solubility parameter values in the range of 7.0 to 9.9 $cal^{1/2}$ $cm^{-3/2}$. The maximum swelling of 62% was with cyclohexane. Compared with the polyethylene discussed below, also a crystalline material, the swelling was generally somewhat higher, but still in the same range of solubility parameter values.

Polyethylene

Six different PE compositions, all of which were commercial FMLs, were included in this swelling study: one LLDPE, one low-density polyethylene (LDPE), three HDPEs, and an alloy of HDPE and EPDM. These materials showed a substantial difference in crystallinity and density, as shown in Table 10. The greatest swelling was in organics with Hildebrand solubility parameter values in the range of 7.0 to 9.9 $cal^{1/2}$ $cm^{-3/2}$. None of these FMLs disintegrated in the test; the maximum swelling was 41% for the HDPE-A in tetrachloroethylene. The values of swelling more or less followed the crystallinity values and showed the importance of crystallinity in the swelling. As the solubility parameter is a property of the amorphous phase of a polymer, crystallinity does not affect the solubility parameter values of these FMLs; consequently, their solubility parameters should be close.

TABLE 10. POLYETHYLENES STUDIED IN SWELLING EXPERIMENT

Grade of polyethylene	Matrecon identification number	Density, g/cm^3	Carbon black, %	MP[a], °C	Crystallinity, %	Ash, %
Low density	309A	0.938[b]	0.8	110	38.4	1.6
Linear low-density	284	0.929	1.7	128	39.1	0.7
High-density	184	0.951	2.0	134	69.3	<0.1
	263	0.953	...	...	...	...
	305	0.945	2.9	126	63.9	0.7
High-density alloyed with EPDM	181	0.949	4.0[b]	131	41.8	0.3

[a] MP = melting point.

[b] May contain a small amount of char.

Polyurethane

A single PU, which was a commercial product being considered for secondary containment applications, was included in this swelling study because of its known resistance to oils. This PU was a TP which disintegrated in six of the 30 organics. The disintegration and large swelling was in organics with solubility parameter values in the range of 9.6 to 11.9 cal$^{1/2}$ cm$^{-3/2}$. The low swelling in the octanes confirms the known low swelling of this type of polymer in petroleum oils and fuels.

Polyvinyl Chloride

Four PVC compositions were included in the swelling study. Three were commercial FMLs represented by a regular PVC FML (Liner No. 153), an elasticized PVC (Liner No. 176R), and an oil-resistant PVC (Liner No. 144). The fourth PVC was a laboratory-prepared composition containing 40% di(ethylhexyl) phthalate as the plasticizer, and was similar in basic composition to the regular PVC FML (Liner No. 153). These compositions swelled highly or disintegrated in organics that had solubility parameter values in the range of 8.3 to 13.9 cal$^{1/2}$ cm$^{-3/2}$.

The volume swelling of the commercial PVC FML (Liner No. 153) differed from that of the laboratory-prepared PVC FML-type composition (DPQ). The commercial regular PVC FML disintegrated in six of the organics and the laboratory-prepared composition disintegrated in 11 of the organics. The differences probably resulted from the different types of PVC used in each.

The elasticized PVC had a considerably different swelling behavior than the regular PVC. The PVC-OR showed low swelling in the octanes but dissolved in the ketones and in two of the three nitrogen-based organics.

Summary of Discussion of the Swelling Results

The swelling data presented in Appendix C indicate that the FML compositional factors that relate to the magnitude of swelling of the different FMLs after immersion in the organics or water are, in decreasing order of importance, as follows:

- Crystallinity content.
- Solubility parameters of FML in comparison with solubility parameters of solvent.
- Crosslink density.
- Filler content.
- Plasticizer content.
- Miscellaneous factors (e.g. changes in composition with time such as antioxidant loss).

As indicated in Table 11, all of the polymeric compositions in the study were either wholly amorphous, e.g. the rubbers and PVC, or partially amorphous, e.g. HDPE, which is semicrystalline. Among the amorphous polymeric compositions some, such as CPE and PVC, were uncrosslinked and others, such as the rubber compositions, were crosslinked. At least nine of the compositions were partially crystalline, e.g. the PEs; the degree of crystallinity varied from approximately 70% for one of the HDPEs to probably less than 5% for one of the polyester elastomers. The materials tested in this study represent the range of materials currently available as FMLs. In the course of this study, neither the degree of crystallinity nor the crosslink density was thoroughly quantified.

The data in Appendix C show the great range of the effects of immersion in organics on the polymeric compositions. Swelling ranged from a minor fraction of a percent to disintegration. Within the range of materials in the study, the degree of crystallinity appears to have the greatest effect on the level of swelling. All of the materials that contained some crystallinity, i.e. the PEs, PB, PELs, and possibly the EVA, showed comparatively low swelling, and none, except for one of the PELs, disintegrated in m-cresol. The swelling of the PEs ranged from a fraction of a percent to a maximum of 25%. The HDPE swelled the least, and the alloy of HDPE and EPDM swelled the most; it should be noted that the rubber phase of the alloy is amorphous and uncrosslinked. The PB, also partially crystalline, had a maximum swelling of 62% in cyclohexane and had a median swelling of 5%. Immersion of the EVA, which probably contains some crystallinity, resulted in significantly low swelling values; none of the organics in the study caused it to disintegrate. Some PELs, which as a class of materials vary considerably in composition, can have crystallinity. Of the two PELs that were tested, the one identified as Liner No. 323 had pronounced crystallinity and swelled significantly less than the second (Liner No. 316). However, in spite of its apparent crystallinity Liner No. 323 disintegrated in m-cresol.

The proximity of the solubility parameters of the amorphous phase of a polymeric composition and the solubility parameters of a solvent appears to be the second most significant factor in the swelling of a polymeric composition. For a given amorphous and uncrosslinked polymeric FML, swelling could range from a few percent to hundreds of percent and even to disintegration or dissolution in organics having solubility parameters close to that of the polymer in the FML.

The crosslinking of an amorphous polymer prevents the disintegration of a polymeric composition on exposure to an organic; however, it does not prevent great swelling if the polymer and the organic have close solubility parameters. The level of swelling of amorphous materials immersed in an organic will be affected by the level of crosslinking. This conclusion is supported by the data on crosslinked polymers, particularly on the lightly crosslinked compositions that were prepared in the laboratory, when compared with data on the uncrosslinked compositions. The level of crosslinking in the compositions tested in this study were not quantified. Quantification would require preparation of special compounds and the measurement of crosslinking densities.

Nine compositions containing fillers were included in this study. All of these compositions were amorphous and three were crosslinked. It should be noted that even though some compositions such as the PEs contain small levels of carbon black (i.e. 2 to 3% by weight), they are not considered "filled." As fillers do not swell in the presence of organics, they can reduce the swelling of a composition. The degree to which swelling will be reduced depends on the amount and physical and chemical structure of the filler that is used. Fillers that chemically bond to the polymer reduce swelling further. In the formulation of gasket compositions and other compositions that may contact oils and organics, high levels of filler are often used to reduce the swelling. One of the tested CSPE compositions was prepared for this study with a known level of carbon black. The results showed that in those organics that resulted in relatively low swelling of all of the CSPE composition (i.e. in organics that had solubility parameters that were not close to those of the CSPE), the composition filled with carbon black swelled significantly less than an unfilled control which had a somewhat higher level of crosslinking. However, in those organics that caused considerable swelling in the control, the carbon-black-filled composition disintegrated, probably reflecting the lack of bonding between the carbon black and the polymer.

The plasticized compositions, such as the PVCs and the CPEs, resulted in a wide range of swelling values depending on the plasticizer and the organic in which the composition was immersed. The plasticizer or plasticizers can be extracted during service and replaced by portions of the fluid medium in

TABLE 11. SUMMARY[a] OF IMMERSION OF FMLS AND RELATED COMPOSITIONS IN ORGANICS AND WATER

Compositions in study		Features of compositions, number of compositions					Effect of immersion	
Basic polymer type	Number of different compositions tested	Contains amorphous domains	Contains crosslinks	Contains crystalline domains	Contains fillers	Contains plasticizers	Number of samples disintegrated[b]	Range of swelling, %
Chlorinated polyethylene	3	3	0	0	3	3	18	1.7- ∞
Chlorosulfonated polyethylene	6	6	1	0	3	2	8	3.0- ∞
Epichlorohydrin rubber	1	1	1	0	1	1	0	0.5-184
Ethylene propylene rubber	1	1	1	0	1	1	0	0.0-146
Ethylene vinyl acetate	1	1	0	1[c]	0	0	0	0.7-250
Neoprene	1	1	1	0	1	1	0	0.1-181
Nitrile rubber	1	1	1	0	0	0	1[d]	9.2-700
Polyester elastomer								
PEL with lower or no crystallinity	1	1	0	?[e]	0	0	2[f]	2.4- ∞
PEL with greater crystallinity	1	1	0	1	0	0	1[g]	0.7-25
Polybutylene	1	1	0	1	0	0	0	0.2-62
Polyethylene	6	6	0	6	0	0	0	0.1-41
Polyurethane	1	1	?[h]	0	0	0	6	1.7- ∞
Polyvinyl chloride	4	4	0	0	0	4	32	0.6- ∞
Total	28	28	5	9	9	12	66	

[a] From Appendix C.

[b] In 30 organics and in water; 31 samples were immersed per composition tested.

[c] Probably contains some crystallinity; however, crystallinity was not quantified.

[d] The nitrile rubber sample disintegrated in m-cresol only.

[e] May contain some crystallinity; however, crystallinity was not quantified.

[f] PEL (Liner No. 316) disintegrated in m-cresol and trichloroethylene.

[g] PEL (Liner No. 323) disintegrated in m-cresol only; the next greatest swelling was 25.1% in TCE.

[h] May contain some crosslinking; however, crosslink density was not quantified.

which it is immersed to yield little change in the properties of the composition. This requires that the plasticizer be soluble in the medium and that the polymer be insoluble. In the PVC compositions that were studied, a large number disintegrated by dissolution due to the solubility of the amorphous PVC in many of the organics.

TREATMENT OF THE SWELLING DATA TO CALCULATE SOLUBILITY PARAMETERS

After considering several methods of determining the individual solubility parameters of the polymeric compositions from the swelling data, it was decided to calculate them by fitting the data to a nonlinear curve which would be a good model for the swelling of the polymeric composition versus the solubility parameter of the organic. A continuous curve with a symmetrical peak such as shown in Figure 2 was desired. The Lorentzian peak shape, which has been used in curve fitting of nuclear magnetic resonance and spectral data, appeared to be the most suitable for this application. These data have shape requirements similar to solubility data. The general function of the curve is:

$$L(x) = \frac{a}{1 + b\,(x - c)^2}$$

in which the variables are:

$L(x)$ = swelling of the polymer in percent increase in volume;

x = solubility parameter of the organics;

and in which the parameters are:

a = maximum height of the peak in percent increase in volume;

$b = 1/(\text{peak width})^2$, where the peak width is in $\text{cal}^{1/2}\ \text{cm}^{-3/2}$ (width, $1/\sqrt{b}$, is the distance between the peak location and the point where the intensity is at 1/2 of its maximum);

c = the peak location in $\text{cal}^{1/2}\ \text{cm}^{-3/2}$.

ASYST® software (Adaptable Laboratory Software, 1985) was used to fit this curve to the data. This program employs an iterative process to select the parameters and develop a curve fit. In this procedure a nonlinear least squares algorithm was used. The ASYST® software has three different routines from which to choose in fitting data to a nonlinear curve: the Gauss-Newton procedure, the BFGS procedure, and a combination of the two. The third procedure appeared to be the most appropriate and was used.

The curve-fitting procedure was applied individually to each of the 28 FMLs and other polymeric compositions to calculate each of the four solubility parameters using the individual solubility parameters of all of the organics that were used in the swelling test. The results of the calculations are presented in Table 12. Typical curves for each of the solubility parameters are presented in Figures 4 through 11. The swelling data and the

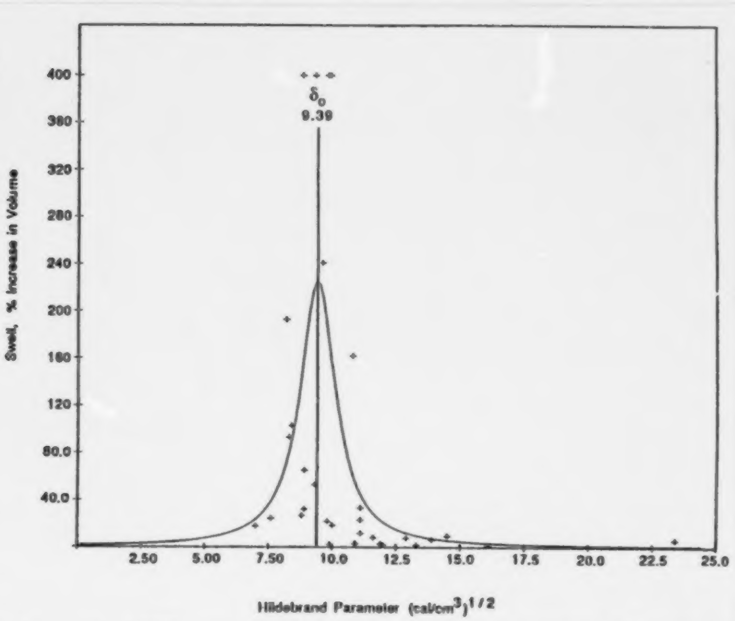

Figure 4. Swelling of CSPE composition DPO, with peroxide cure and without filler or plasticizer, as a function of the Hildebrand solubility parameter of each of 31 organics.

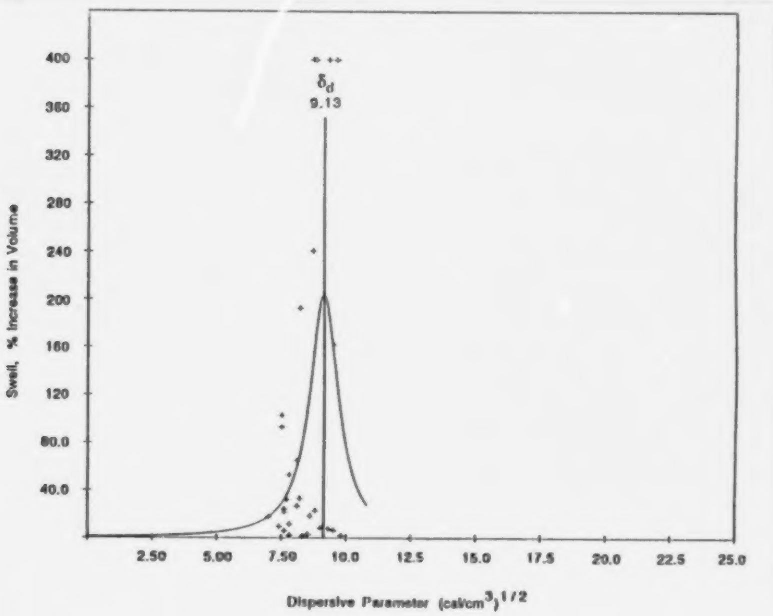

Figure 5. Swelling of CSPE composition DPO, with peroxide cure and without filler or plasticizer, as a function of the dispersive solubility parameter of each of 31 organics.

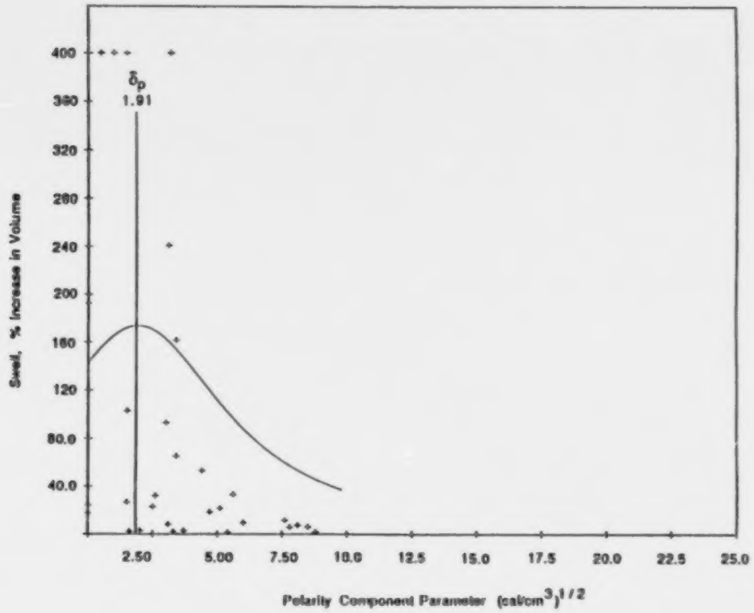

Figure 6. Swelling of CSPE composition DPO, with peroxide cure and without filler or plasticizer, as a function of the polarity solubility parameter of each of 31 organics.

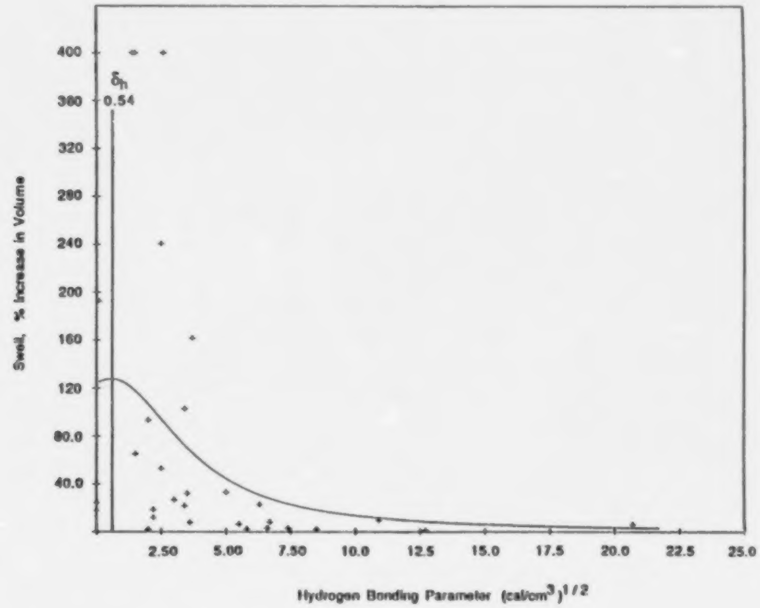

Figure 7. Swelling of CSPE composition DPO, with peroxide cure and without filler or plasticizer, as a function of the hydrogen-bonding solubility parameter of each of 31 organics.

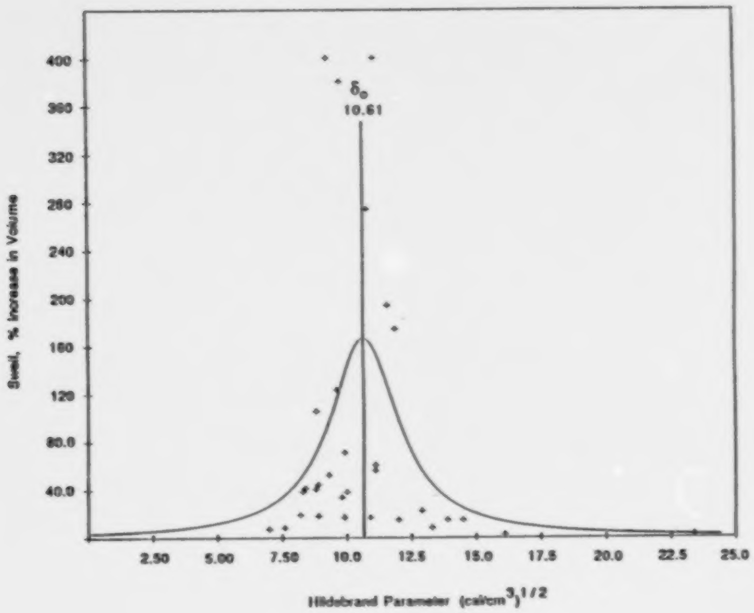

Figure 8. Swelling of polyester elastomer (Liner No. 316) as a function of the Hildebrand solubility parameter of each of 31 organics.

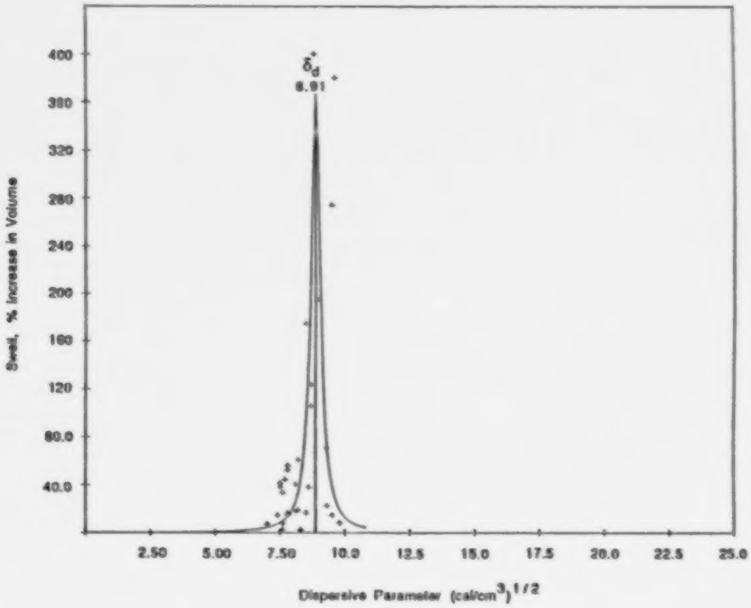

Figure 9. Swelling of polyester elastomer (Liner No. 316) as a function of the dispersive solubility parameter of each of 31 organics.

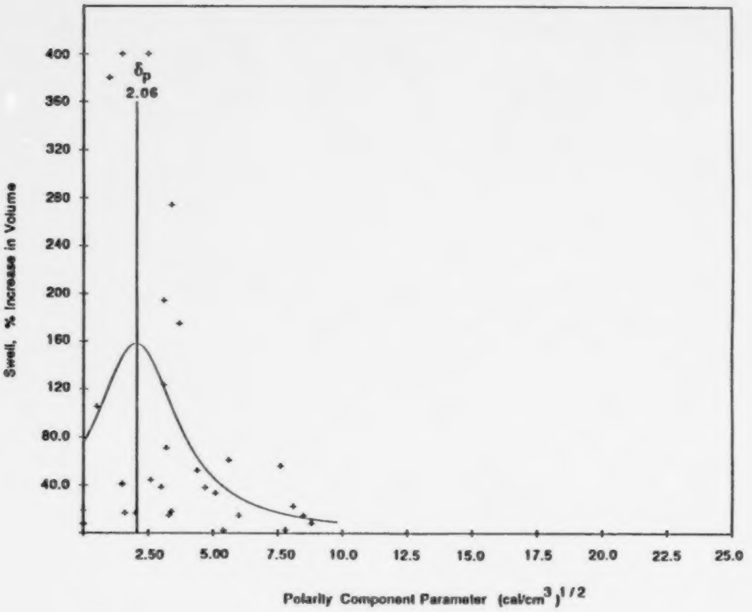

Figure 10. Swelling of polyester elastomer (Liner No. 316) as a function of the polarity solubility parameter of each of 31 organics.

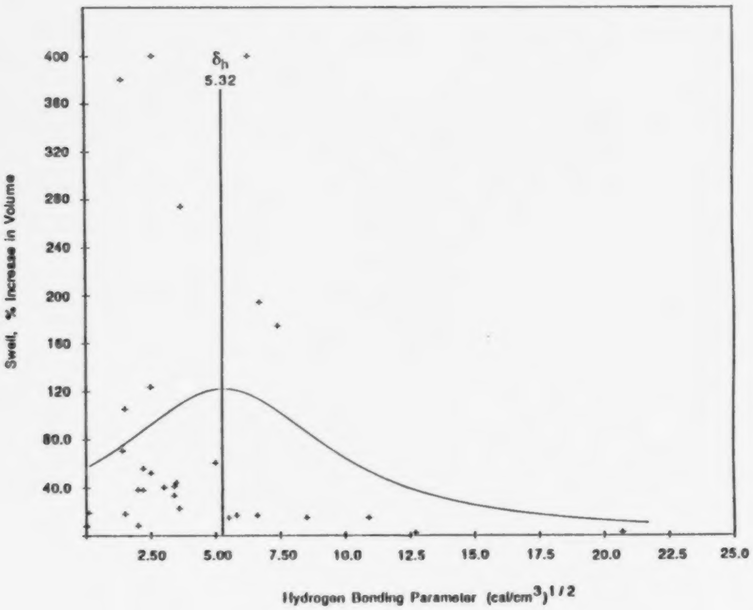

Figure 11. Swelling of polyester elastomer (Liner No. 316) as a function of the hydrogen bonding solubility parameter of each of 31 organics.

TABLE 12. SOLUBILITY PARAMETER VALUES FOR FMLS AND OTHER POLYMERIC COMPOSITIONS

Polymer	Matrecon identification number	$(cal/cm^3)^{1/2}$					
		δ_o	δ_d	δ_p	δ_h	δ_t[a]	Δ[b]
Chlorinated polyethylene	195	9.27	7.99	3.23	3.15	9.18	-0.09
	335R	9.39	9.23	2.06	2.50	9.78	+0.39
	378R	8.91	9.23	2.84	3.15	10.2	+1.29
Chlorosulfonated polyethylene	169R	9.52	9.13	0.93	2.60	9.54	-0.02
	174R	9.39	8.91	1.76	1.52	9.21	-0.18
	DOY-3[c]	9.39	9.07	1.03	1.19	9.21	-0.18
	DOZ-2[c]	9.27	9.18	1.91	1.38	9.48	+0.21
	DPO[c]	9.39	9.13	1.91	0.53	9.34	-0.05
	DPP[c]	9.39	9.13	1.96	1.09	9.40	+0.01
Epichlorohydrin rubber	178	11.35	9.23	5.00	4.56	11.45	+0.10
		11.35	9.23	5.54	4.56	11.69	+0.34
Ethylene propylene rubber	232	8.91	9.07	0.64	0.65	9.12	+0.21
Ethylene vinyl acetate	308A	9.39	8.96	0.88	0.98	9.06	-0.33
Neoprene	168	9.52	9.29	1.72	1.95	9.65	+0.13
Nitrile rubber	DPN[c]	10.49	9.02	2.50	3.58	10.02	-0.47
Polyester elastomer	316	10.61	8.91	2.06	5.32	10.58	-0.03
	323	11.35	8.91	4.02	4.12	10.61	-0.74
Polybutylene	221A	7.69	7.49	0.05	0.43	7.50	-0.18
Polyethylene:							
Low-density	309A	7.81	9.45	0.05	0.11	9.45	+1.64
Linear low-density	284	8.17	9.02	0.05	0.43	9.03	+0.86
High-density	184	7.44	9.29	0.05	0.65	9.31	+1.87
	263	7.93	8.05	0.05	0.98	8.11	+0.18
	305	7.56	8.50	0.05	0.54	8.52	+0.96
HDPE/EPDM-alloy	181	7.69	9.07	0.15	0.76	9.10	+1.41
Polyurethane	351	11.59	8.86	3.82	5.64	11.18	-1.63
Polyvinyl chloride	153	10.13	7.99	5.39	3.91	10.40	+0.27
	DPQ[c]	9.64	7.83	5.64	4.34	10.58	+0.94
Elasticized polyvinyl chloride	176R	9.76	9.34	4.26	3.47	10.84	+1.09
Polyvinyl chloride (oil-resistant)	144	9.64	7.88	4.41	4.23	9.97	+0.33

[a] $\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$.

[b] $\Delta = \delta_t - \delta_o$.

[c] Laboratory-prepared compound, the composition of which is presented in Appendix A.

fitted curves are shown on each figure. In order to test the data obtained from the curve for the Hildebrand and component solubility parameter values, a total solubility parameter was calculated from the square root of the sum of the squares of the dispersive, polarity, and hydrogen-bonding component parameters. The calculated total solubility parameter values are compared with the Hildebrand solubility parameter values, which were calculated separately, and are also presented in Table 12. They should be essentially equal; overall, the agreement between the two values for a given polymeric compound was within a few tenths of the solubility parameter unit, $cal^{1/2}$ $cm^{-3/2}$, and most were within half a solubility parameter unit, though there are a few that were outside that difference.

Among those results with which the agreement between the calculated total parameter and the Hildebrand solubility parameter values was not as good as expected were those for PE and PB. In these cases, the curve peaks for some of the component parameters were broad and not well defined. These low swelling values reflect the high crystallinity and low amorphous phase contents of these polymeric compositions. The crystalline phase does not swell and, at the same time, may restrict the swelling in the amorphous domains that are near.

DISCUSSION OF SOLUBILITY PARAMETERS

A goal of this study was to develop the component solubility parameters of FMLs to use in predicting the effect upon a specific FML proposed for use with a specific waste liquid, the composition of which would be known. The component solubility parameter data given in Table 12 for specific FMLs were "tested" with specific organics that had been used in the immersion testing to determine the magnitude of swelling that might occur with the combination. After considering the factors of crystallinity and crosslinking in some of the FMLs, it was found that, in many cases, the swelling of the FML was not predictable from the component solubility parameters of the FML and the organic by the proximity of their respective solubility parameter values.

It was also observed that some of the organics, for example the aliphatic alcohols, swelled at considerably lower levels than was anticipated based upon their component solubility parameters. This can be observed by an inspection of the data in Appendix C. It was also observed that there was a difference between aliphatic alcohols and the aromatic and aliphatic ring-structured alcohols. Those alcohols based on aliphatic chains swelled the PEL composition considerably less than did the two ring-structured alcohols, benzyl alcohol and furfuryl alcohol, even though their component solubility parameters have similar values.

Results such as those described above indicate that factors beyond the solubility parameters are involved in estimating the swelling of specific highly amorphous polymers with specific organics, and that specific testing should be performed on organics which differ in general type from those used in this study.

SECTION 6

DISTRIBUTION OF ORGANICS BETWEEN WATER AND FMLS

INTRODUCTION

The distribution of a dissolved substance between two phases that are essentially immiscible has been an important subject for study in chemistry for more than a century. Some of the early investigations showed that at equilibrium the ratio of the concentrations of a substance dissolved in two immiscible solvents in contact with one another is constant and does not depend upon the relative volumes of the solutions involved. Later studies showed that the distribution would be constant only if a single molecular species was being considered as being distributed between the two phases, that is, the molecular species would be the same in both phases and would not either dissociate or associate when transferring from one phase to the other. Thus, the partitioning could be treated by classical thermodynamics as an equilibrium process and would be related to other commonly measured functions such as partial pressure, osmotic pressure, and chemical potential. The partitioning of a dissolved substance, for example, between water and an organic such as toluene, forms the basis for the separation of organic compounds by extraction. When there are more than two or more immiscible phases, an organic solute, for example, will partition or distribute itself among phases depending upon its solubility in the different phases. Most organic solutes will tend to be more soluble in the organic phase and remain in that phase unless the solute is exceptionally soluble in water. Nevertheless, a small amount of the organic will exist in water when the two phases are in contact. The ratio at which the distribution of the solute takes place is termed the partitioning or the distribution coefficient and is considered to be the ratio of the dissolved substance in the organic phase over that in the water phase.

The concept of partitioning is being used in tracking pollutants and contaminants in the environment, e.g. pesticides and various organics which resist biodegradation, including the polychlorinated biphenyls (PCBs) (Neely et al, 1974). These chemical species can move through the food chain, resulting in higher concentrations at each trophic level. This process which reflects the greater solubility of an organic chemical in oily tissue than in water has been termed "bioconcentration." The process of partitioning is also involved in spill cleanup processes in which polymeric materials that are used to absorb a spilled organic, e.g. an oil, can then be disposed of in an environmentally safe manner.

In waste disposal containment, a similar situation exists with respect to polymeric FMLs and waste liquids that contain dissolved organic substances. The organics dissolved in the waste liquids can partition between the waste liquid and the liner and thus enter and swell the liner. The organic can then permeate and be transported through the liner at a rate which depends on the material, its thickness, the temperature, and the concentration gradient across the liner. Inasmuch as the FMLs are organic and are at least partially amorphous, they can behave much like liquids from a thermodynamic standpoint. The degree of solubility of the solutes will depend upon the relative solubility parameters of the solute and the FML.

In previous work, Haxo et al (1985a) observed that slightly soluble organics dissolved in aqueous waste liquids can partition to an FML with which the liquid is in contact. This work was performed with dilute but saturated aqueous solutions of tri-n-butyl phosphate (TBP) at less than 0.10% concentration, that is, less than 1,000 mg/L. The weights of FML specimens immersed in a dilute solution of TBP reached an equilibrium. The time required to reach equilibrium depended on the FML and, in some cases, equilibrium was reached after several years. The amount of TBP absorbed at equilibrium also depended on the type of FML. It should be noted that TBP has a molecular weight of 266.3 and a relatively low volatility.

Immersion testing of the FMLs was also performed in neat TBP (Haxo et al, 1985b). In that experiment, the absorption of the TBP to equilibrium by various lining materials took place in a relatively short time and, in most cases, ended at considerably higher absorption values than the values in the tests with the saturated solutions, indicating an effect of concentration.

An important technique used in the experimental work presented in this section was gas chromatography (GC). Appendix D describes the equipment, materials, and conditions used in the GC analyses. Appendix E presents information on all the organics used in these studies. Included in this information are source, purity, molecular weight, etc. Many of the organics used in the experimental work are identified by the EPA as volatile contaminants. A complete list of the organics presently identified by the EPA as volatile contaminants is presented in Appendix F.

PRELIMINARY STUDIES OF THE DISTRIBUTION OF ORGANICS BETWEEN ORGANIC PHASES AND WATER

As a preliminary part of the research on this project, a study was initiated to determine the level and rates of swelling that take place when FMLs are immersed in dilute solutions of different concentrations of volatile organics that are encountered in waste streams. Because of the lower molecular weight of volatile organics, the effects were expected to take place in relatively short times. These initial experiments, which were performed to study the effects preparatory to more extensive studies, included the following:

- Partitioning of a mixture of organics having different solubility parameters, between the organic phase and water.

- Partitioning between a mixture of organics in an aqueous solution and a paraffinic oil, Nujol. Direct GC analysis of the Nujol was made to determine the volatile organics that had been absorbed by it.

- Partitioning of a mixture of organics dissolved in an aqueous solution and an HDPE sample that had been immersed in the liquid. GC headspace analysis of exposed HDPE was performed to determine the actual amount and type of organics that were absorbed from the organics mixture in water.

Partitioning Between a Mixture of Organics and Water

In this experiment, a mixture of equal weights of seven organics was mixed in different ratios with water. The organics consisted of acetone, MEK, TCA, TCE, benzene, toluene, and mixed xylenes, as shown in Table 13. This mixture of organics was added to deionized water in three volume ratios: 1:99, 10:90, and 50:50. Each organic-water mixture was shaken and allowed to equilibrate and the respective volumes of the organics and aqueous phases were determined. The aqueous and organic phases were analyzed by GC, and the results are presented in Table 14. These results show that the organics partitioned into the water at different concentrations depending on the ratio of the organic phase to the water. At the 1:99 and 10:90 volume ratios, the organic phase was higher in specific gravity than the aqueous phase and settled to the bottom. In the 50:50 mixture, the organic phase was lighter than the aqueous phase and rose to the top.

TABLE 13. COMPOSITION OF THE ORGANIC MIXTURE USED IN PARTITIONING EXPERIMENT WITH WATER

Organic	Specific gravity	Weight ratio in mixture	Volume ratio in mixture
Acetone	0.791	1	1.264
Methyl ethyl ketone	0.805	1	1.242
1,1,1-Trichloroethane	1.346	1	0.743
Trichloroethylene	1.462	1	0.684
Benzene	0.869	1	1.151
Toluene	0.866	1	1.154
Xylenes (mixture of o-, m-, and p-)	0.868	1	1.152
Mixture of above organics	0.947	7	7.390

TABLE 14. DISTRIBUTION OF SEVEN ORGANICS IN MIXTURE BETWEEN ORGANICS AND AQUEOUS PHASES

Organic	Organic:water ratio[a] 1:99 (volume basis)			Organic:water ratio[a] 10:90 (volume basis)			Organic:water ratio[a] 50:50 (volume basis)		
		Distribution ratio[b]			Distribution ratio[b]			Distribution ratio[b]	
	Amount added, g	Organic phase, %	Aqueous phase, %	Amount added, g	Organic phase, %	Aqueous phase, %	Amount added, g	Organic phase, %	Aqueous phase, %
Acetone	0.135	∿0.5	...	1.35	∿9.1	∿127	6.75	∿16.3	∿33.2
Methyl ethyl ketone	0.135	∿4.4	...	1.35	∿16.6	∿110	6.75	∿15.6	∿27.4
1,1,1-Trichloroethane	0.135	∿58.2	12.9	1.35	76.2	2.2	6.75	106.3	0.7
Trichloroethylene	0.135	84.4	10.3	1.35	85.6	1.5	6.75	103.0	0.4
Benzene	0.135	76.4	19.7	1.35	89.2	2.8	6.75	114.1	0.6
Toluene	0.135	92.4	7.1	1.35	92.3	1.1	6.75	105.6	0.2
Xylenes (mixture of o-, m-, and p)	0.135	98.7	12.1	1.35	93.9	0.7	6.75	101.0	0.2
Total	0.947			9.47			47.25		
		Volume of organics and water in the phases, mL							
Volume of phase observed		0.60	99.4		7.0	93.0		44.0	56.0
Organics calculated[c]		0.56	0.59		6.26	4.13		37.65	5.26
Water calculated[d]		0.04	98.8		0.74	88.9		6.35	50.7

[a] Ratio of the total organics to water when mixed.

[b] Percent of the organic in each phase after the combination of organics and water had been mixed and allowed to settle. The data are based on the GC analyses of each phase; in many cases, the sum did not add up to 100%.

[c] Calculated from the GC analysis.

[d] The water volume in the organic phase was calculated from the determined organics volume and the measured phase volume.

Partitioning of Organics Between an Aqueous Solution and Nujol

Assessment of the partitioning of organics in an aqueous solution between water and a solid polymer such as HDPE can be performed using headspace GC analysis of an exposed FML sample that has absorbed volatile organics to identify and quantify the individual organics. Using a liquid similar in chemistry to a specific solid polymer can also be used to measure more directly the partitioning of organics between an aqueous solution and that polymer. Nujol is a paraffinic oil chemically similar to polyethylene, though of much lower molecular weight and completely amorphous. Thus, it was used as a model for the polyethylene. A partitioning experiment was set up in which two ratios of water to oil were investigated:

- A 50:50 water:oil combination.

- A 90:10 water:oil combination.

In addition, two different organic mixtures were added to these combinations; the first was a spiking mixture used in other experiments, and the second was a mixture of organics based on the recorded individual solubilities of aromatic and chlorinated hydrocarbons in water. In both cases, the organic mixture was added to the water:oil combination, which was then shaken and allowed to settle and equilibrate. After separation and equilibration, each of the phases was sampled and injected into the GC to measure the organics content.

The composition of the two organic mixtures and the results of the two experiments are presented in Table 15. In the experiment with the 50:50 water:oil combination, the MEK and methyl alcohol entered the water phase, and the aromatics, the TCE, and most of the TCA entered the Nujol. The composition of the organic mixture added to the 90:10 water:oil mixture was based on the reported solubilities of the individual constituents in water. The amount of organics added to this water:oil mixture was considerably higher than that added to the 50:50 mixture. In this experiment, most of the acetone and MEK entered the water phase with a small amount of benzene and toluene. The oil phase contained a small amount of acetone and MEK and the remaining constituents of the original organics mixture. These results again show that the organics tend to migrate toward those components that have similar solubility parameters.

Partitioning of Organics Between an Aqueous Solution and an HDPE FML

The absorption by an FML of the organics in a waste liquid can be measured by determining the volatiles by gas chromatography or gas chromatography-mass spectrographic analysis. Pyroprobe techniques, such as the one described by Haxo (1983), are not sufficiently accurate for quantitative analytical purposes.

TABLE 15. PARTITIONING OF A MIXTURE OF VOLATILE ORGANICS BETWEEN WATER AND A PARAFFINIC OIL[a]

	Mixture									
	50:50 Water:oil combination[b]					90:10 Water:oil combination[c]				
	Initial mixture[d],	Aqueous phase		Oil phase		Initial mixture[e],	Aqueous phase		Oil phase	
Organic	mg/L	mg/L	%	mg/L	%	mg/L	mg/L	%	mg/L	%
Acetone	...	...	...	...	...	711	698	98.2	13	1.8
Methyl alcohol	650	650	100	∼0	∼0	...	...	...	...	...
Methyl ethyl ketone	650	650	100	∼0	∼0	725	671	92.5	54	7.5
1,1,1-Trichloroethane	650	<20	<3.2	>630	>96.8	1206	∼0	∼0	1206	100
Trichloroethylene	500	∼0	∼0	500	100	1188	∼0	∼0	1188	100
Benzene	900	∼0	∼0	900	100	1584	175	11.0	1409	89.0
Toluene	350	∼0	∼0	350	100	468	6.3	1.3	462	98.7
Xylenes	65	∼0	∼0	65	100	125	∼0	∼0	125	100

[a] Nujol. Plough, Inc., Memphis, Tennessee.

[b] 13 mL water:13 mL oil.

[c] 100 mL water:11.1 mL oil.

[d] A mixture used in a previous experiment.

[e] Composition of the mixture was based upon reported solubilities of individual constituents in water at 25°C.

Headspace GC (HSGC) can be used to measure the volatile organics that are absorbed by an FML during immersion and compatibility testing of FMLs by using the following procedure:

- A small specimen (ca. 1.5 to 2.5 g) of an exposed FML is taken from a test solution or vapor and placed in a small vapor-tight can provided with a septum through which vapors from the specimen can be sampled.

- The can is placed in an oven at 105°C, and heated for about an hour.

- A sample of the vapor is drawn from the can and injected into the GC.

- The sample is placed in a new can which is heated in a 105°C oven for about an hour.

- A sample of the vapor is injected into the GC. This step is repeated until no organics show in the GC.

After this procedure has been completed, the organics concentration in the compatibility test solution is compared to the total organics evaporated from the FML specimen. The conditions of the GC analysis are described in Appendix D (Set of Conditions 1).

In a typical experiment, an HDPE sample that had been exposed to a test solution containing TCA, TCE, benzene, toluene, and xylenes in the concentrations shown in Table 16 was analyzed for volatile organics by HSGC in accordance with the procedure described above. The HDPE sample was heated in a total of four cans. The results of this analysis are presented in Tables 16 and 17.

These results show that the organics tested partition to the FML phase to yield concentrations manyfold greater than the concentrations in the aqueous solutions. For example, the concentration of the xylenes in the HDPE was 62 times the concentration in the aqueous phase. It should be noted that the acetone and MEK that were present in the original waste liquid were not detected in the GC of the vapors from the HDPE sample in the headspace GC analysis.

DISTRIBUTION OF ORGANICS BETWEEN ORGANIC-SATURATED WATER AND A POLYETHYLENE FML

To assess the distribution of dissolved organics between an aqueous solution and FMLs, a series of saturated aqueous solutions, each containing a single organic, were prepared with an excess of organics and placed in vapor-tight jars. Since acetone, which was in this series, is miscible with water at all proportions, the aqueous solution was prepared at 250,000 mg of acetone per L of solution.

A specimen of polyethylene (100-mil HDPE, Liner No. 483) was immersed in each jar. Data on selected properties are presented in Table 18). At intervals, the specimens were removed and weighed until each had reached a maximum value; the concentration of the organic in the FML specimen was calculated and reported in mg of organic per L of solution, i.e. per L of FML. The values used for the concentrations of the organics in the saturated aqueous solutions, which were assumed to be concentrations at saturation, were obtained from the literature (Riddick and Bunger, 1970). The distribution coefficients (D_{LW}), i.e. the ratio of the concentration of the organic in the FML (C_{FML}) to the concentration in the aqueous solution (C_{H_2O}), were calculated. The results of the analyses and calculations are presented in Table 19.

TABLE 16. PARTITIONING OF VOLATILE ORGANICS FROM AQUEOUS LEACHATE TO IMMERSED HDPE

Organic	Initial concentration in leachate, mg/L	Organics in exposed HDPE[a]		Concentration in HDPE divided by concentration in leachate
		Head-space, mg	Concentration in HDPE[b], mg/L	
1,1,1-Trichloroethane	250	22.6	9,650	40x
Trichloroethylene	250	27.7	11,820	47x
Benzene	125	4.0	1,710	14x
Toluene	125	12.9	5,510	45x
Xylenes (mixture of o-, m-, and p-)	125	17.6	7,510	62x
Total	875	084.8	36,200	41x

[a] Exposed HDPE specimen in test was 2.3433 g before 110°C headspace heating and 2.2735 g after 19.5 h heating, for a volatiles loss of 0.0698 g or 2.98% of the initial weight.

[b] See Table 17.

In all cases, more than 30 days were required for the specimen to reach maximum swelling. The time required to reach maximum swelling ranged from 30 days for the specimen immersed in benzene solution to 52 days for the specimen immersed in the TCE solution. The distribution of all of the organics, except the acetone and MEK, were predominantly to the HDPE specimens. The distribution coefficients ranged from 54 for benzene to 422 for o-xylene. In the case of the acetone and MEK, the small increases in the weight of the polyethylene FML specimens indicated that the amount of organic that exceeded the solubility of the organic in water appeared to have been absorbed by the FML.

TABLE 17. HEADSPACE GC ANALYSIS OF HDPE AFTER IMMERSION IN A SPIKED LEACHATE[a]

	Headspace can and cumulative headspace time[b]								
	One 0.92 h		Two 1.89 h		Three 18.3 h		Four 19.5 h		Total 19.5 h
Organic	Amount[c]	Extent of volatization, %	Amount[c]	Extent of volatization, %	Amount[c]	Extent of volatization, %	Amount[c]	Extent of volatization, %	Amount[c]
1,1,1-Trichloroethane	0.448	37.9	0.387	70.4	0.350	100	0	100	1.185
Trichloroethylene	0.512	53.1	0.320	86.3	0.132	100	0	100	0.964
Benzene	0.107	62.5	0.051	92.5	0.013	100	0	100	0.171
Toluene	0.277	50.4	0.175	82.2	0.090	98.4	0.009	100	0.551
Xylenes	0.277	36.9	0.277	73.8	0.184	98.3	0.012	100	0.750
Total	1.621	44.8	1.210	78.2	0.769	99.5	0.012	100	3.621

[a] Concentration of "spike" in leachate in mg/L was 1,1,1-TCA, 250; TCE, 250; benzene, 125; toluene, 125; xylene, 125.

[b] Headspace cans were friction-topped 0.5-gal cans with septum; they were conditioned for use by 110°C oven heating for more than 1 hour, followed by air jet flushing of the interior.

[c] Weight percent of organic found in the headspace, based upon the initial weight of the test specimen, i.e. 2.3433 grams.

TABLE 18. SELECTED PROPERTY VALUES OF A 100-MIL HDPE FML (LINER NO. 483)

Property	Value
Thickness, mil	100
Volatiles, %	0.1
Carbon black content, %	2.5
Density:	
FML (as received), g/mL	0.945
Polyethylene (calculated by correcting for carbon black content), g/mL	0.936
Crystallinity, %	59
Melting point, °C	121

The data show that, when dissolved in water that is in contact with FMLs, the organics in the series that are slightly soluble in both water and FMLs will distribute predominantly to the FML.

DISTRIBUTION OF ORGANICS BETWEEN A SATURATED POLYETHYLENE FML AND DEIONIZED WATER

An experiment complementary to that described in the previous subsection was performed. In this experiment specimens of the same polyethylene (100-mil HDPE, Liner No. 483) were individually saturated with each of the same organics and then immersed in DI water in separate vapor-tight jars. The respective concentrations of the organics in the water were monitored with time by sampling and GC analysis until they had reached maximum values which indicated equilibrium had been established.

In this test, vapor-tight containers were prepared consisting of 8-oz glass jars with ground and polished-top edges, Teflon-lined phenolic resin tops, each fitted with a Swagelock sampling port and Teflon-lined silicone rubber septums. Prior to use, the tops were tested by HSGC for leaks with a matched jar to ensure that seals were obtained (Figure 12).

Specimens 3 x 1 in. (approximately 2 g) were first immersed in the respective organics and weighed daily until they did not change in weight. The times to reach maximum swelling values were considerably shorter than the times in the experiments with the saturated aqueous solutions. With the five aromatic organics in this test, the time to maximum weight was approximately one week. The remaining four organics, i.e. acetone, MEK, TCA, and TCE, required 15 to 21 days to reach maximum swelling. Some of the differences probably can be attributed to laboratory temperature variation. A comparison of the swelling in neat organics with that in saturated aqueous solutions of the same organics is presented in Table 20. The maximum swelling values

TABLE 19. DISTRIBUTION OF NINE ORGANICS BETWEEN SATURATED WATER SOLUTIONS AND A POLYETHYLENE FML[a]

Organic	Density of organic, g/mL	Solubility in water at room temperature[b] (C_{H_2O}), mg/L	Time to maximum swelling, days	Weight increase of HDPE FML specimen, %	Concentration of organic in swollen FML (C_{FML}), mg/L	Distribution coefficient (D_{LW}), C_{FML}/C_{H_2O}	Logarithm of distribution coefficient, Log D_{LW}
Acetone	0.788	250,000[c]	44	0.33	3,210	0.0128	-1.891
Methyl ethyl ketone	0.805	240,000	46	0.62	5,900	0.0246	-1.609
Trichloroethylene	1.464	1,100	43	16.71	144,200	131.0	2.11
1,1,1-Trichloroethane	1.339	1,320	52	11.70	103,000	78.2	1.89
Benzene	0.879	1,180	30	7.22	63,900	54.3	1.73
Toluene	0.866	515	50	8.05	70,600	137	2.13
o-Xylene	0.897	175	40	8.42	73,800	422	2.62
m-Xylene	0.868	196	38	8.19	71,800	366	2.56
p-Xylene	0.854	190	49	8.43	73,600	387	2.58

[a] HDPE FML (Liner No. 483).

[b] Values obtained from Riddick and Bunger (1970).

[c] Initial concentration of the acetone-water solution; acetone is miscible with water in all proportions.

obtained in the neat organics were approximately equal to those obtained in the saturated organic solutions, but all were somewhat higher. Table 21 presents the swelling results on a volume basis, which corrects for the difference in density of the organics and the density of the polyethylene FML.

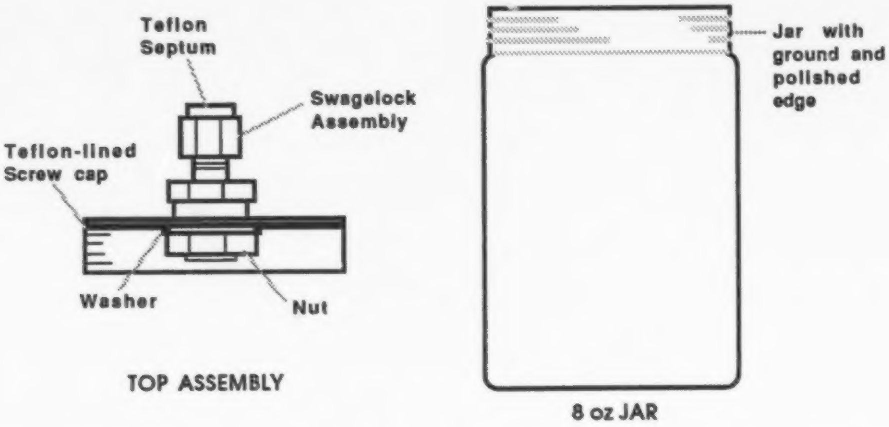
Teflon Septum
Swagelock Assembly
Teflon-lined Screw cap
Washer
Nut
TOP ASSEMBLY
Jar with ground and polished edge
8 oz JAR

Figure 12. Schematic of the immersion test jar with septum for withdrawing samples of water for GC analysis.

TABLE 20. COMPARISON OF THE SWELLING OF POLYETHYLENE FML[a] IMMERSED IN NEAT ORGANICS AND IN SATURATED AQUEOUS SOLUTION OF ORGANICS

	Neat organic		Saturated aqueous solution	
Organic	Maximum swelling (by weight), %	Time to maximum swelling, d	Maximum swelling, (by weight), %	Time to maximum swelling, d
Acetone[b]	0.96	18	0.33	44
Methyl ethyl ketone	1.83	21	0.62	46
1,1,1-Trichloroethane	12.13	17	11.70	52
Trichloroethylene	17.52	15	16.71	43
Benzene	7.61	6	7.22	30
Toluene	8.40	6	8.05	50
o-Xylene	8.73	9	8.42	40
m-Xylene	8.51	6	8.19	38
p-Xylene	8.72	7	8.43	49

[a] HDPE FML (Liner No. 483).

[b] Acetone is miscible with water in all proportions; the concentration was set at 250,000 mg/L for the experiment with the aqueous solution.

TABLE 21. EQUILIBRIUM SWELLING ON WEIGHT AND VOLUME BASES OF HDPE[a] IN NEAT ORGANICS

Organic	Specific gravity	Specific volume, mL/g	Swelling (by weight), %	Swelling (by volume), %
Acetone	0.791	1.264	0.96	1.27
Methyl ethyl ketone	0.805	1.242	1.83	1.63
Trichloroethylene	1.466	0.682	17.52	12.70
1,1,1-Trichloroethane	1.346	0.743	12.13	9.51
Benzene	0.879	1.138	7.61	9.32
Toluene	0.866	1.155	8.40	10.27
o-Xylene	0.880	1.136	8.73	10.58
m-Xylene	0.864	1.157	8.53	10.53
p-Xylene	0.861	1.161	8.72	10.87

[a] HDPE FML (Liner No. 483), the density of which was 0.945 g cm^{-3}.

After equilibrium was reached the swollen specimens were placed in the small containers (Figure 12) that had been filled with DI water with minimum headspace above the water. The water in the jars was sampled periodically and analyzed by GC for the organics absorbed by the FML specimens. The water was sampled with a 1-µL syringe at 5-min. intervals and then hourly after immersion of the saturated HDPE specimen. The 1-µL sample size was sufficient for analyzing the water for an organic by GC with negligible loss of liquid from the container. The concentration, in mg/L, of the organic in the water was determined using a calibration curve which was generated from standard aqueous solutions of each of the organics. The GC conditions are presented in Appendix D. Concentrations in these tests were determined under Set of Conditions 2. This procedure was continued until the concentration of the organic in the water had reached a maximum value, at which time the specimen was withdrawn and weighed. At that time the concentration of the organic remaining in the specimen was determined by HSGC.

Data on the weight at maximum swelling of the specimen at saturation as well as the weight of the swollen specimen after equilibrating with the water in the jars, and the time required to reach equilibrium are presented in Table 22. The rate at which the absorbed organics diffused out of the FML into the water varied considerably. It took 24 hours for the FML specimen containing TCE to reach an equilibrium concentration, whereas the specimen containing the benzene required 120 hours. It does not appear that equilibrium had been reached with acetone and MEK when the specimens were withdrawn.

The distribution coefficients, also presented in Table 22, show the strong tendency of the chlorinated and aromatic organics to remain in the polyethylene FML (Liner No. 483).

DISTRIBUTION OF ORGANICS FROM A DILUTE SOLUTION INTO TWO COMPARTMENTS SEPARATED BY AN FML

The experiments described in the previous three subsections demonstrated that organics in dilute aqueous solutions (e.g. leachates) differ in their distributions between the solution and the FML with which it is in contact. Solubility of an organic in a barrier such as an FML is a first and necessary condition for permeation of the organics through the FML. The organic must first dissolve in the FML before it can diffuse and permeate through the FML. As discussed in Sections 4 and 5, the solubility of an organic in an FML can be predicted by their respective solubility parameters.

The next step in determining the relationship between organics in aqueous solutions and FMLs was to determine the rate at which organic compounds are partitioned from dilute aqueous solutions into an FML and then transmitted through the liner into the airspace on the opposite side. This is a situation encountered by an FML in service at a hazardous waste impoundment containing aqueous/organic leachate.

Transmission of a Mixture of Nine Organics in Dilute Aqueous Solution Through a Linear Low-Density Polyethylene FML

An exploratory experiment was conducted to assess the distribution of organics in dilute solutions and their transmission through an FML. A special apparatus was constructed consisting of two compartments which were fabricated of aluminum (Figure 13). A port was incorporated low in the bottom compartment and several holes were drilled in the wall of the upper compartment through which sampling could be performed. The holes were covered with an aluminum-backed tape through which the samples could be withdrawn and which could reseal the holes after each sampling.

In this experiment, an aqueous solution containing nine different organics at low concentrations, such as might be encountered in a leachate, was placed in the upper compartment of the two-compartment apparatus and was separated from the lower compartment by a polyethylene FML. The upper compartment was filled with 1,600 mL of DI water which was spiked with the mixture of nine organics. The lower compartment was an airspace which was sampled for the organics that permeated through the liner. The FML used in this experiment was a 31-mil LLDPE FML (Liner No. 345), selected data on which are reported in Table 23.

The nine organics used in this experiment and their sources, purities, and solubilities in water are presented in Table 24. They are volatile organics commonly found in leachates and are known to cause swelling and changes in the properties of FMLs with which they come in contact. The organics include chlorinated hydrocarbons (TCE and TCA), polar oxygenated solvents (acetone and MEK), and aromatic hydrocarbons (benzene, toluene, and

TABLE 22. DISTRIBUTION OF ORGANICS BETWEEN AN ORGANIC SATURATED FML[a] AND DEIONIZED WATER

	Saturated FML		At equilibrium in deionized water					
Organic	Maximum swelling (by weight), %	Concentration of organic, mg/L	Time to maximum concentration in H_2O, hours	Swelling of FML (by weight), %	Concentration of organic in FML (C_{FML}), mg/L	Concentration of organic in water (C_{H_2O}), mg/L	Distribution coefficient (D_{LW}), C_{FML}/C_{H_2O}	Logarithm of distribution coefficient, Log D_{LW}
Acetone	0.96	9,080	~120[b]	0.62	5,830	35	167	2.22
Methyl ethyl ketone	1.83	17,120	~120[b]	0.91	8,990	127	71	1.84
Trichloroethylene	17.52	150,500	24	8.98	84,800	966	88	1.94
1,1,1-Trichloroethane	12.13	106,700	50	6.91	65,800	589	112	2.04
Benzene	7.61	67,100	120	1.95	19,030	643	30	1.47
Toluene	8.40	73,400	46	4.42	42,000	266	158	2.19
o-Xylene	8.73	76,300	52	7.07	65,600	186	352	2.54
m-Xylene	8.51	74,300	78	6.70	62,200	193	322	2.50
p-Xylene	8.72	75,900	58	6.93	64,300	165	390	2.59

[a] HDPE FML (Liner No. 483).

[b] Equilibrium did not appear to have been reached when specimen was removed from test at 120 hours.

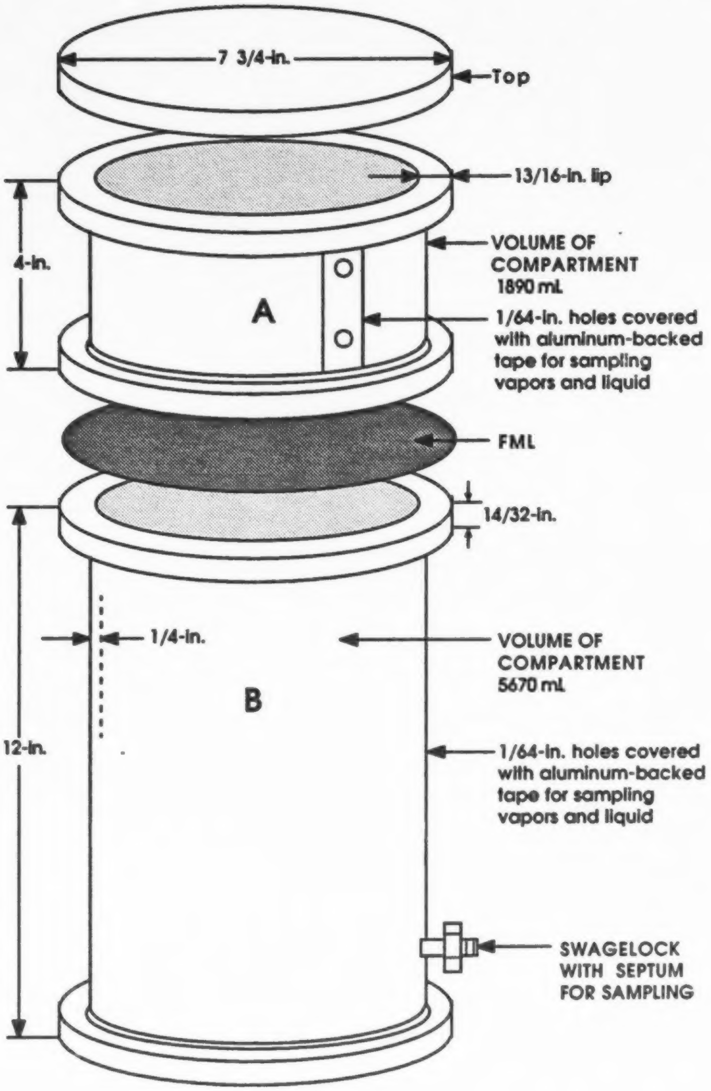
7 3/4-in.
Top
13/16-in. lip
4-in.
VOLUME OF COMPARTMENT 1890 mL
A
1/64-in. holes covered with aluminum-backed tape for sampling vapors and liquid
FML
14/32-in.
1/4-in.
VOLUME OF COMPARTMENT 5670 mL
B
12-in.
1/64-in. holes covered with aluminum-backed tape for sampling vapors and liquid
SWAGELOCK WITH SEPTUM FOR SAMPLING

Figure 13. Two-compartment apparatus for measuring distribution and transmission of organics through an FML. Volume of the top compartment (A) was 1,890 mL and the volume of the bottom compartment (B) was 5,670 mL. Inside diameter of the compartment is 6 1/16 in. (15.4 cm).

TABLE 23. SELECTED PROPERTY VALUES OF LLDPE FML (LINER NO. 345)

Property	Value
Thickness, mil	31
Carbon black content, %	2.5
Density	
FML	0.926
Polyethylene (calculated by correcting for carbon black content)	0.915

TABLE 24. ORGANICS IN DEIONIZED WATER IN THE TOP COMPARTMENT OF THE TEST APPARATUS

Compound	Source	Purity, %	Solubility in water[a], mg/L	Solubility parameter, δ_0
Acetone	Mallinckrodt	99.98	miscible	9.9
Methyl ethyl ketone	Mallinckrodt	99.98	240,000	9.3
1,1,1,-Trichloroethane	MCB[b]	99.9	1,320	8.6
Trichloroethylene	Mallinckrodt	99.9	1,100	9.2
Benzene	EM Science	99.9	1,780	9.2
Toluene	Mallinckrodt	99.9	515	8.9
o-Xylene	J. T. Baker	99	175	8.8
m-Xylene	MCB[b]	98	196	8.6
p-Xylene	Spectrum Chemicals	98+	190	8.6

[a] Weight percent soluble in saturated solution at 25°C.

[b] Matheson, Coleman, and Bell.

o-, m-, and p-xylenes). These organics have been identified as volatile contaminants by the EPA (Appendix F).

Equal weights (57.5 mg each) of the nine organics were mixed together. This mixture was added by syringe to the top compartment of the test apparatus, which contained 1.6 L DI water. The water was in direct contact with the liner (Figure 13). The volume of the airspace above the water was 290 mL (Table 25).

TABLE 25. ZONES IN TWO-COMPARTMENT TEST APPARATUS

Zone	Compartment	Description	Volume, mL
1	Top	Headspace above the solution of organics	290
2	Top	Dilute aqueous solution of organics	1,600
3	Barrier between the top and bottom	FML (30-mil LLDPE): Portion exposed to liquid	14.7
4	Bottom	Airspace below the FML	5,670
		Total volume	7,575

The components of the four zones or phases in the assembled test apparatus are described in Table 25. They consist of the headspace above the water containing the organics, the water solution containing the organics, the FML barrier, and the airspace below the barrier.

Zones 1, 2, and 4 were monitored periodically. GC analysis was performed on samples withdrawn from the two airspaces and the water solution. HSGC was performed on the FML when the test was finished at 190 hours and the apparatus was dismantled. The procedure for the GC analyses is described in Appendix D (Set of Conditions 3).

The results of the GC analyses are presented in Tables 26 and 27. Table 26 presents the distribution of the organics in the various zones at the end of the exposure when the apparatus was dismantled. Data are presented as amounts by weight of the individual organics. A materials balance was made to determine the amount of each organic that could be accounted for, based on the amounts that were dissolved in the DI water at the beginning of the experiment. The final concentrations of the individual organics in each zone are presented in Table 27. It should be noted that only 65% of the initial amounts of the two chlorinated organics (TCE and TCA) added to the apparatus were accounted for in the final analyses of the contents of all

TABLE 26. FINAL DISTRIBUTION OF THE ORGANICS IN THE FOUR ZONES OF THE TWO-COMPARTMENT TEST APPARATUS[a]

		Zone 1	Zone 2	Zone 3	Zone 4		
Compound	Initial[b] weight in water, mg	Weight in airspace[c] above FML, mg	Final weight in water[d], mg	Weight in FML[e], mg	Weight in airspace below FML[f], mg	Total, mg	Fraction accounted for, %
Acetone	57.5	5.0	42.1	0	0	47.1	81.9
Methyl ethyl ketone	57.5	4.1	51.3	0	0	55.4	96.3
1,1,1-Trichloroethane	57.5	8.0	21.0	8.0	0	37.0	64.3
Trichloroethylene	57.5	12.0	6.0	7.0	12.48	37.5	65.1
Benzene	57.5	12.75	11.0	4.0	24.74	52.49	91.4
Toluene	57.5	18.7	14.7	11.52	9.68	54.6	94.9
m- and p-Xylene	115.0	5.7	60.1	18.05	11.16	90.01	82.6
o-Xylene	57.5	3.8	38.1	11.08	6.0	58.98	102.0
Total	517.5	77.05	244.3	59.55	64.06	438.08	84.63

[a] After 190 h of operation at room temperature.

[b] 0.5175 g of equal weight solution of nine organics in 1606 g of deionized water.

[c] The volume of the airspace was 290 mL.

[d] The volume of the water was 1,600 mL.

[e] The volume of the FML in the area exposed to the aqueous solution was 14.70 mL.

[f] The volume of the airspace below the FML was 5,670 mL.

zones. Also, approximately 82% of the acetone and the m- and p-xylenes were accounted for and, overall, 85% of the organics were accounted for in the final analysis. The results indicate that there were losses of organics during the test, some of which were due to the sampling.

TABLE 27. FINAL CONCENTRATIONS OF THE ORGANICS IN THE FOUR ZONES OF THE TWO-COMPARTMENT TEST APPARATUS[a],[b]

	Zone 1	Zone 2	Zone 3	Zone 4	
Compound	Concentration in air-space above aqueous solution, mg/L	Concentration in aqueous solution (C_{H_2O}), mg/L	Concentration in FML (C_{FML})[c], mg/L	Concentration in air-space below FML, mg/L	Ratio of C_{FML}/C_{H_2O}
Acetone	19.3	26.3	0	0	0
Methyl ethyl ketone	15.8	32.0	0	0	0
1,1,1-Trichloroethane	31.0	13.1	419	0	31.9
Trichloroethylene	46.5	3.7	367	2.2	99.1
Benzene	49.4	6.8	209	4.3	30.7
Toluene	72.4	9.1	603	1.7	66.3
m- and p-Xylene	22.0	37.5	946	1.96	25.2
o-Xylene	14.7	23.8	580	1.05	24.3

[a] After 190 h of operation at room temperature.

[b] Initial concentration of each organic in the aqueous solution was 35.9 mg/L. The concentrations of m- and p-xylenes were also 35.9 mg/L each, but they could not be separated by the GC column and, therefore, are combined in this table.

[c] Based on a volume of 14.70 mL for the FML exposed to dilute aqueous solution of organics.

The apparatus was subsequently leak-tested by pressurizing it under water. It was found that, when the apparatus was closed in a way similar to that used in the test, there were small leaks at the top and bottom covers of the apparatus.

In spite of the apparent loss of a minor fraction of the organics, some valid observations can be made as to the distribution of the organics between the aqueous solution and the FML, and as to the permeation of the FML by the organics.

Of the nine individual organics, three (i.e. acetone, MEK, and TCA) were not observed in the airspace below the FML barrier. In addition, neither acetone nor MEK was observed in the FML in HSGC analysis. Both were retained primarily in the aqueous solution, although some of each (approximately 10%) entered the airspace above the dilute aqueous solution (Table 26).

In view of the great difference in the volumes of the zones (e.g. Zone 1 was 290 mL; Zone 2 was 1,600 mL) that were incorporated in the test, data on the concentrations of the individual organics can yield a different picture than weight distribution data. For example, the concentrations of the chlorinated organics (TCE and TCA) and of the more volatile aromatics (benzene and toluene) were substantially higher than their respective concentrations in the water. Also, the concentration of the individual organics in the airspace above the dilute aqueous solution was higher for TCE, benzene, and toluene (Table 27).

The concentration of the organics in the airspace below the liner was significantly lower than in the other zones of the test apparatus, which indicates the retarding effect of the FML on the rates of transmission. It is believed that complete equilibrium had not been achieved when the apparatus was dismantled to measure the concentration of the organics in the FML.

Distribution and Transmission of TCE in Two-Compartment Test Apparatus with LLDPE FML as a Barrier

In view of the apparent leakage of vapor from the two-compartment test apparatus described above, the experiment was repeated with a single organic. TCE was selected because it is volatile and appeared to have been lost from the test apparatus in the previous experiment. Only 65% of the initial TCE that was added to the apparatus could be accounted for in the previous experiment.

Before starting the experiment with TCE, a preliminary experiment was run to determine whether the apparatus could be sealed more successfully using a sealing tape. The apparatus was assembled using a Teflon tape, such as that used with threaded pipe fittings, as a seal for the top and bottom of the test apparatus. No leaks were observed when the assembled apparatus was pressurized under water.

The apparatus was set up using a five-zone configuration instead of the four-zone configuration used in the previous experiment. In this experiment water was placed in the bottom compartment. The zones and their appropriate volumes are described in Table 28. Ports were introduced in both the top and bottom compartments so that all zones, except for the FML, could be sampled while the experiment was running.

TABLE 28. CONFIGURATION OF THE FIVE ZONES IN TWO-COMPARTMENT TEST APPARATUS

Zone	Compartment	Description	Volume, mL
1	Top	Airspace above aqueous solution of organics	848
2	Top	Aqueous solution of organics	1,042
3	Barrier between the top and bottom	FML (31-mil LLDPE): Area exposed to solution	~15[a]
4	Bottom	Airspace below the FML	5,067
5	Bottom	Deionized water	603
		Total volume	7,575

[a] Volume varies with the thickness of the FML. The volume of a 30-mil FML exposed to the aqueous solution is about 15 mL.

After beginning the test, the effectiveness of the GC column was destroyed when injecting water solutions for analysis, and a replacement had to be obtained; therefore, data for aqueous solutions, as a function of time, could not be obtained until the third day. The two airspaces were monitored, however, and after 120 hours the apparatus was dismantled to check on the tightness of the seal. An HSGC analysis was performed on the FML. The GC conditions are described in Appendix D (Set of Conditions 4).

Table 29 presents the results of the analyses of the vapor, liquid, and FML of the five zones during and at the time the test apparatus was dismantled. The data include both the amounts and the concentration of the TCE in the various zones. In the 120 hours of exposure, a summation of the amounts that were observed in each of the zones was 477 mg; thus, 91.6% of the original 521 mg that were injected into the DI water were accounted for in the final analysis. The results indicate that there was probably no leak from the test apparatus during the second experiment and that the Teflon tape had corrected the leak observed in the first experiment.

During the 120 hours of the test the concentration of the TCE in the water dropped from 500 mg/L to 144.5 mg/L. Approximately 120 mg were absorbed by the FML and another 160 mg were transmitted through the FML into the bottom compartment. The concentration of the TCE in the water in the bottom compartment was 100 mg/L; thus the concentration of the TCE in the water in the bottom compartment approached that of the TCE in the water above the FML. As in the previous experiments, there was a preponderant migration of this organic to the FML. At the same time, the concentration of the TCE in the FML increased to approximately 56 times that in the water above the liner. At that time the FML had absorbed about 0.5% of its weight in TCE.

TABLE 29. DISTRIBUTION OF TRICHLOROETHYLENE IN TWO-COMPARTMENT TEST APPARATUS

Zone				Start of test		At 24 hours		At 45 hours		At end of test, 120 hours	
No.	Description	Volume, mL	Organic	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L
1	Airspace above the aqueous solution of organics	848	TCE	0	0	67.8	80.0	54.1	63.9	48.5	57.2
2	Aqueous solution of organics	1,042	TCE	521	500	...	...	...	...	150.7	144.5
3	FML barrier (LLDPE-Liner No. 284)	14.70	TCE	0	0	...	...	...	...	119.2	8109
4	Airspace above DI water in bottom compartment	5,067	TCE	0	0	139.8	27.6	152	30.0	98.0	19.3
5	DI water in bottom compartment	603	TCE	0	0	...	...	...	...	60.7	100.6
	Total	7,574.7		521						477.1	
	Fraction accounted for, %			100						91.6	

DISTRIBUTION OF TWO ORGANICS IN A TEST APPARATUS CONSISTING OF THREE COMPARTMENTS SEPARATED BY POLYETHYLENE FMLS

The experiments performed in the two-compartment test apparatus demonstrated the feasibility of this type of apparatus in assessing the transmission of organics from dilute aqueous solutions through polymeric FMLs. These experiments indicated the substantial difference between organics as related to their solubility in the polymeric FML.

In order to simulate an FML in service more accurately, a three-compartment closed apparatus was designed. The design of this apparatus is shown schematically in Figure 14. In this design, the covers of one end of each of the top and the bottom compartments were welded to the walls to avoid potential loss of volatiles. The only potential leaks were those that might occur at the flanges between which the FML specimens that separated the three compartments were mounted. Ports with Teflon silicone rubber septums were incorporated in each of the three compartments for use in withdrawing samples for GC analysis from the aqueous and airspace zones (Table 30). The two FML zones could be analyzed by GC after the apparatus was dismantled.

The three-compartment apparatus simulates the configuration of a covered landfill as follows:

- The airspace in the top compartment is like the airspace over a "cover" liner. The FML specimen between the top and middle compartments is like a "cover" liner.

- The airspace in the middle compartment simulates the headspace above a waste liquid, and the dilute solution containing organics serves as the waste liquid. The FML specimen between the middle and bottom compartments simulates the service conditions of a bottom liner.

- The airspace and the deionized water in the bottom compartment simulate, respectively, pore spaces in the soil and the groundwater.

The configuration of the zones within each compartment can be modified to assess double liners and various auxiliary materials, such as covers, geotextiles, and drainage materials.

In the first experiment of this series, only two organics were dissolved in the test liquid, i.e. toluene and TCE. Both of these organics are commonly found in leachates and are easily identifiable and trackable by GC analysis. Information on these two organics is presented in Appendix E. Both are identified as volatile contaminants by the EPA (Appendix F). An LLDPE FML (Liner No. 284) was used in this experiment and separated the three compartments. Data on this FML are presented in Table 31.

In this experiment seven zones were incorporated in the three compartments. Zone 4 was filled with 500 mL DI water and spiked with 191 mg each of toluene and TCE to yield concentrations of 382 mg each per L of water. The

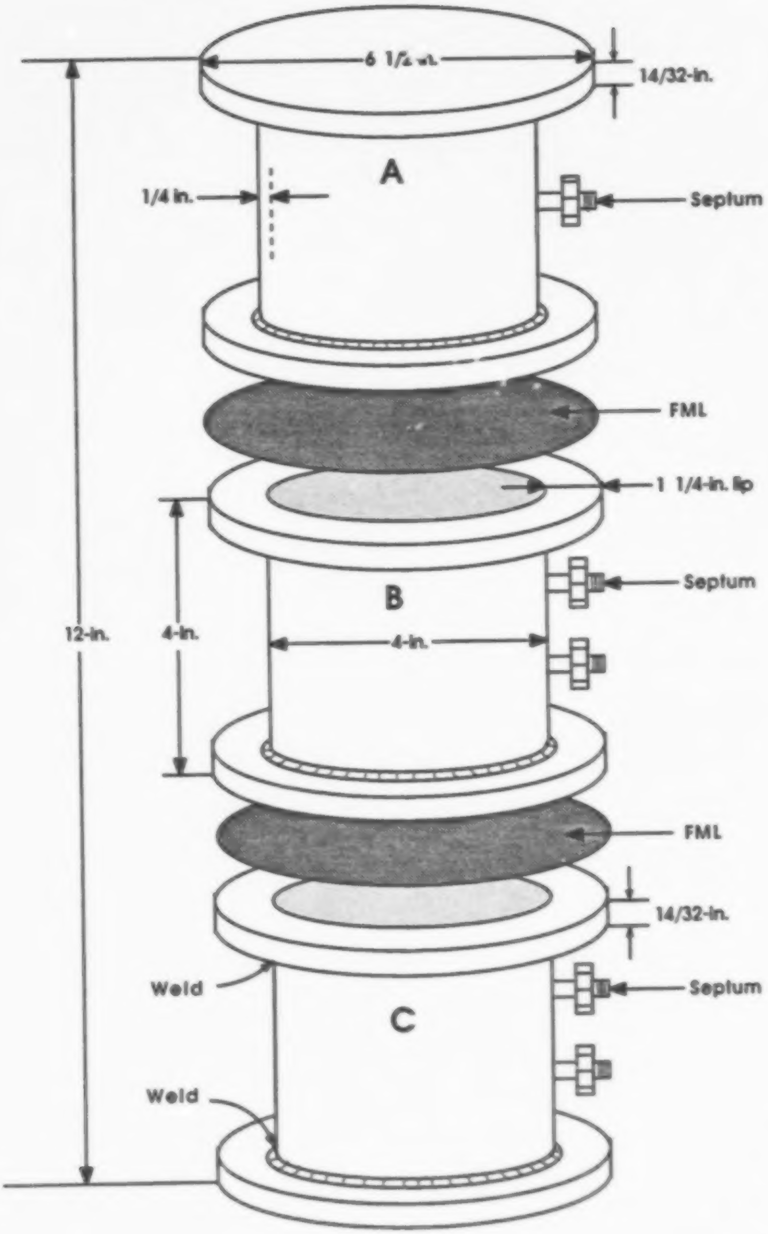
6 1/4 in.
14/32-in.
A
1/4 in.
Septum
FML
1 1/4-in. lip
B
Septum
12-in.
4-in.
4-in.
FML
14/32-in.
Weld
Septum
C
Weld

Figure 14. Schematic of the three-compartment test apparatus used in the study of water/FML distribution and permeation of organics from dilute solutions. Inside diameter of the compartment was 4 inches.

TABLE 30. ZONES IN THREE-COMPARTMENT TEST APPARATUS

Zone	Compartment	Description	Volume, mL
1	Top	Airspace above "cover"	806
2	Barrier between top and middle	"Cover" FML (33-mil LLDPE): Area exposed to solution	~7
3	Middle	Airspace above aqueous solution containing organics	306
4	Middle	Dilute aqueous solution containing organics	500
5	Between middle and bottom	"Bottom liner" (33-mil LLDPE): Area exposed to solution	~7
6	Bottom	Airspace below "bottom liner" FML	506
7	Bottom	Deionized water	300
		Total	2,432

TABLE 31. SELECTED PROPERTY VALUES OF A 33-MIL LLDPE FML (LINER NO. 284)

Property	Value
Thickness, mil	33.4
Carbon black content, %	2.5
Specific gravity of FML	0.927
Density:	
FML at 23°C, g/mL	0.924
Polyethylene (calculated by correcting for carbon black content), g/mL	0.913
Crystallinity, %	36.3
Melting point, °C	119

five zones containing water or vapor were sampled and analyzed by GC periodically to assess the changes in concentrations in these zones. After 256 hours, when the concentrations appeared to remain constant, the apparatus was dismantled and the FML samples were removed and analyzed by HSGC to determine the concentrations of the organics in the FMLs. The conditions of the GC analyses are presented in Appendix D (Set of Conditions 5). Also, analysis was performed separately on the FML in the flange area, as well as the area that contacted the vapor. The results of the analyses of samples taken at 24, 96, and 256 hours are reported in Table 32.

The results show that that water in Zone 7 in the bottom compartment had absorbed organics. At the end of the test, for both toluene and TCE, the concentrations were the same in both aqueous zones, i.e. in Zone 4 and in the bottom compartment, demonstrating the transport of these organics through the FML and airspace to the water at the bottom. The data also show that, for each of the two organics, the concentrations in the airspaces in Zones 1, 3, and 6 were similar in value and the concentrations in the two FML specimens were essentially equal. Overall, 92.6% of the TCE and 97.7% of the toluene were accounted for in the final analyses of all zones.

The HSGC analysis of the FML in the flange area showed no organics, which indicated that there was no leakage through the flanges. Overall, these results show that the apparatus had come to equilibrium; they also show the high absorption of organics by the FML. At these equilibrium conditions, the distribution coefficients for TCE and toluene were 178 and 120, respectively, in the LLDPE FML.

DISTRIBUTION OF SIX ORGANICS IN A TEST APPARATUS CONSISTING OF THREE COMPARTMENTS SEPARATED BY FMLS

Another experiment was performed using the same type of test apparatus, configuration of zones, and the same polyethylene FML (LLDPE, Liner No. 284). In this experiment, 191 mg each of six organics were injected into the water in the middle compartment in Zone 4; they were n-octane, TCE, toluene, o-xylene, n-butanol, and propionic acid. Table 33 presents data on these organics, including their solubilities in water, their concentrations in the solution, and their respective Hildebrand solubility parameters. More information on these organics is presented in Appendix E. Due to the low solubility of n-octane in water, a large excess of this organic was added to the water.

The five zones that contained either liquid or vapor were monitored by sampling and analysis by GC (see Appendix D, Set of Conditions 6 for the GC conditions). Exposure in the test apparatus was continued until essentially no change took place in the concentrations of these chemicals in any given zone. At 28 days, the analyses indicated that concentrations of the toluene and TCE had leveled, at which time the test apparatus was dismantled and the FMLs were analyzed by HSGC for the organics that they had absorbed. The results, which include concentration data for 24 h, 96 h, and 28 d, are presented in Table 34.

TABLE 32. DISTRIBUTION OF ORGANICS IN THREE-COMPARTMENT TEST APPARATUS SEPARATED BY POLYETHYLENE FMLS

Zone				Start of test		At 24 hours		At 96 hours		At end of test, 256 hours	
No.	Description	Volume, mL	Organic	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L
1	Airspace above "cover" FML[b]	806	TCE[a]	0	0	9.2	11.5	14.1	17.5	12.9	16.0
			Toluene	0	0	7.9	9.8	10.0	12.5	4.8	6.0
2	"Cover" polyethylene FML[b]	7.02	TCE	0	0	...	...	...	...	56.1	7,991
			Toluene	0	0	...	...	...	...	60.2	8,575
3	Airspace above test liquid	306	TCE	0	0	12.1	39.5	8.8	29.0	5.97	19.5
			Toluene	0	0	10.1	33.0	8.1	26.5	1.83	6.0
4	Test liquid	500	TCE	191	381	95	190	80	160	22.5	45.0
			Toluene	191	381	92	185	80	160	35.7	71.4
5	Barrier FML[b]	7.02	TCE	0	...	...	...	...	...	56.1	7,991
			Toluene	0	...	...	...	...	...	60.2	8,575
6	Airspace below FML	506	TCE	0	...	8.6	17.2	11.9	23.5	9.87	19.5
			Toluene	0	...	1.16	2.3	3.74	7.4	2.58	5.1
7	"Groundwater"	300	TCE	0	...	0.75	1.5	6.42	21.4	13.5	45.0
			Toluene	0	...	0	0	4.57	15.2	21.4	71.4
	Total	2,432	TCE	191	381	125.6	...	121	...	176.9	...
			Toluene	191	381	111.1	...	106.4	...	186.7	...
	Fraction accounted for, %		TCE	100		65		63		92.6	
			Toluene	100		58		55		97.7	

[a] Trichloroethylene.

[b] Linear low-density polyethylene FML (Liner No. 284).

TABLE 33. ORGANICS ADDED TO DEIONIZED WATER IN COMPARTMENT TWO OF THREE-COMPARTMENT TEST APPARATUS

Organic	Solubility in water at 25°C, mg/L	Solubility parameter, δ_o	Amount added, mg/L
n-Octane	0.66	7.6	382
o-Xylene	175	8.8	382
Toluene	515	8.9	382
Trichloroethylene	1,100	9.2	382
n-Butanol	74,500	11.4	382
Propionic acid	miscible	10.1-10.5	382

All of the organics, except the n-butanol, could be followed during the exposure and appeared in different zones of the test apparatus in the final analyses performed after 28 d of exposure. Seventy-five to almost 84% of the aliphatic, aromatic, and chlorinated hydrocarbons, and 57% of the propionic acid were accounted for in the final analyses. The n-butanol, which was injected initially was not detected after about a week and appeared to be replaced by n-butyric acid which was detected by GC analysis of the water layers. Based on a total conversion of n-butanol to n-butyric acid, 11.50% of the n-butanol was accounted for as n-butyric acid in the final analyses. A portion of the apparent loss of the organics can probably be attributed to the large number of g/mL samples withdrawn from the test apparatus during the 28 d of exposure for GC analysis to track the organics.

The distribution and transport of each of the organics that were initially placed in the water in Zone 4 are discussed briefly in the following subsections.

n-Octane

The n-octane was injected at a concentration substantially above its solubility in water. It appeared within 24 h in the airspace above the spiked water and was substantially absorbed by the upper FML. In the final analysis, essentially 75% of the spike was concentrated in the upper FML, a small amount was detected in the lower FML, and the remainder was observed in the airspaces, particularly in the upper airspace (Zone 1). Only a trace amount was found in the liquid in the bottom compartment.

The fact that the n-octane did not migrate downwards into the lower FML and into the airspace below the FML can be attributed to its low solubility in water. The absorption of the n-octane by the upper FML is attributed to its solubility in the FML, both of which have essentially the same solubility parameter value.

TABLE 34. DISTRIBUTION OF ORGANICS FROM A DILUTE AQUEOUS SOLUTION IN TEST APPARATUS CONSISTING OF THREE-COMPARTMENTS SEPARATED BY POLYETHYLENE FML BARRIERS

Zone			Start of test		At 24 hours		At 96 hours		At end of test, 672 hours	
Description	Volume, mL	Organic	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L	Amount, mg	Concentration, mg/L
Airspace above "upper" FML[a]	806	n-Octane	0	0	12.1	15	4.8	6	2.58	3.2
		Trichloroethylene	0	0	8.1	10	12.5	15.5	19.3	24.0
		Toluene	0	0	28.3	35.1	8.1	10.0	5.64	7.0
		o-Xylene	0	0	10.7	13.3	4.8	6	4.19	5.2
		Propionic acid	0	0	-----none-----		-----none-----		------none------	
		n-Butanol	0	0	-----none-----		-----none-----		------none------	
"Upper" polyethylene FML[a]	7.02	n-Octane	0	0	Analyzed by headspace GC when the apparatus was dismantled				126.7	18,051
		Trichloroethylene	0	0					37.8	5,885
		Toluene	0	0					49.3	7,024
		o-Xylene	0	0					76.0	10,829
		Propionic acid	0	0					------none------	
		n-Butanol	0	0					------none------	
Airspace above spiked water	306	n-Octane	0	0	2.1	68.0	18.6	61	0.98	3.2
		Trichloroethylene	0	0	12.2	40	4.90	16	6.23	20.1
		Toluene	0	0	11.3	37	3.21	10.5	2.14	7.0
		o-Xylene	0	0	2.1	6.8	1.04	3.4	1.59	5.2
		Propionic acid	0	0	-----none-----		-----none-----		------none------	
		n-Butanol	0	0	-----none-----		-----none-----		------none------	
Spiked water	500	n-Octane	191	382	0.3	1	0.3	1	0.3	1
		Trichloroethylene	191	382	40.1	80.1	20.0	40.1	17.1	34.3
		Toluene	191	382	48.1	96.3	22.5	45	15.0	30.02
		o-Xylene	191	382	----trace-----		----trace-----		0.5	1
		Propionic acid	191	382	106	212	102	204	99.7	199.5
		n-Butanol	191	382	140	230	110	220	------none------	
		n-Butyric acid[b]	0	0	-----none-----		----trace-----		20.75	41.25
Lower polyethylene FML	7.02	n-Octane	0	0	Analyzed by headspace GC when apparatus was dismantled				2.60	370
		Trichloroethylene	0	0					47.60	6,780
		Toluene	0	0					61.15	8,712
		o-Xylene	0	0					76.04	10,833
		Propionic acid	0	0					------none------	
		n-Butanol	0	0					------none------	
Airspace below FML	506	n-Octane	0	0	0	0.0	1.36	2.7	1.29	2.56
		Trichloroethylene	0	0	0.4	0.8	2.6	5.2	14.2	28.2
		Toluene	0	0	0.3	0.6	3.8	6.5	5.0	10.0
		o-Xylene	0	0	2.1	6.8	1.04	3.4	1.59	5.2
		Propionic acid	0	0	...	0.015	0.126	0.25	1.9	3.75
		n-Butanol	0	0	-----none-----		-----none-----		------none------	
Bottom water	300	n-Octane	0	0	-----none-----		----trace-----		------trace------	
		Trichloroethylene	0	0	0.15	0.5	4.23	14.1	20.58	68.6
		Toluene	0	0	-----none-----		0.468	1.56	5.6	18.75
		o-Xylene	0	0	-----none-----		-----none-----		------none-------	
		Propionic acid	0	0	-----none-----		----trace-----		10.1	33.15
		n-Butanol	0	0	-----none-----		-----none-----		------none-------	
		n-Butyric acid[b]	0	0	-----none-----		----trace-----		5.4	18.0
									Total in all zones[c]	
		n-Octane	191						155.03	(81.0)
		Trichloroethylene	191						162.8	(85.2)
		Toluene	191						143.8	(75.3)
		o-Xylene	191						159.93	(83.7)
		Propionic acid	191						109.8	(57.4)
		n-Butanol	191						0	(0)
		n-Butyric acid[b]	0						26.15	(11.52)

[a] Linear low-density polyethylene FML (Liner No. 284).

[b] n-Butanol appeared to have been oxidized to n-butyric acid which was detected in the GC as n-butanol decreased in concentration.

[c] Data in parentheses are the percent of initial organics accounted for in the final analyses.

Trichloroethylene

The spike of the trichloroethylene (TCE) was approximately 1/3 of its solubility in water. Due to its volatility, the TCE was observed quickly in the space above the spiked water in Zone 4 and also in the airspace above the upper FML. In the final analyses, the TCE was present in all zones, although approximately 50% of that detected was in the FMLs; a substantial amount was transported into the liquid in the bottom compartment.

These results show the tendency of the TCE to migrate and to be transported through all phases and reflect the solubility of TCE in water as well as in FMLs. At the end of the test, of the six organics in the study, the TCE had the highest concentration in the water in the bottom compartment. The results also indicate the special need for controlling this organic.

Toluene

The spike of toluene was less than its solubility level in water. Toluene behaved similarly to the TCE, although it did not migrate as rapidly. However, it was in the airspace above the upper FML in essentially the same concentration as the TCE. As with the TCE, the toluene was present only in small quantities (0.3 to 0.4 mg) below the lower FML at the end of 24 hours.

At the time of dismantling, the toluene was present in all seven zones, with approximately 77% of the total in the two FML layers. As with the TCE, it moved through all zones of the test apparatus. The results also indicated that special efforts are needed in controlling this organic.

o-Xylene

The initial spike of o-xylene exceeded its solubility in water by approximately a factor of two, i.e. 382 vs. 175 mg/L, and it was anticipated that the o-xylene would tend to migrate relatively rapidly. It was originally thought that solubility of this xylene in water was 191 mg/mL, which is the solubility of mixed xylenes. The o-xylene appeared to have quickly left the spike as it was detected at significant concentrations (6 to 13 mg/L) in the airspaces; only a trace was detected in the water layer and none in the water in the bottom compartment.

In the final analyses, the o-xylene was concentrated principally in the FMLs; almost all of it had migrated out of the spiked water. Also, the concentration in the airspaces was low in comparison with that in the FMLs, which demonstrates the strong affinity of the o-xylene for the FML and reflects its comparatively low solubility in water.

Propionic Acid

Propionic acid has a high solubility parameter value and is completely miscible with water; therefore, it has a strong affinity for water. Only

57% of the propionic acid that was injected at the beginning of the experiment was accounted for in the final analyses; approximately 75% of that was still in the spiked water and the remainder was detected in the water in the bottom compartment. Some of the propionic acid also was detected in the airspace below the lower FML and above the water in the bottom compartment. None of the propionic acid was detected in the other zones of the test apparatus.

n-Butanol

After the first few days of analyses, no n-butanol was observed in any of the zones. However, n-butyric acid appeared in the analyses, indicating that the n-butanol had been oxidized to n-butyric acid. No butyl propionate appeared in the GC scan; thus, the possibility of esterification of the n-butanol with the propionic acid could be discounted. Assuming that the n-butanol was completely converted to n-butyric acid, 11.5% would have been accounted for as n-butyric acid which was detected only in the aqueous phases.

During the dismantling of the test apparatus, there was considerable pressure in the bottom compartment, which may have been CO_2 generated from the decomposition of the acids; CO_2 cannot be detected by flame ionization detection in the GC. Also, the bottom compartment fabricated of aluminum exhibited some corrosion and darkening of the surface.

DISCUSSION

The experiments on the distribution of organics from dilute solutions show that, even at low concentrations in an aqueous leachate, some of the organics can be highly absorbed by the polymeric membrane liner and can permeate the liner. The amount and rate of absorption and the transport of these species through a polymeric liner is a function of such factors as relative solubility parameters of the FML and the organic, crystallinity of the FML, and molecular weight and concentration of the organic constituent. A multi-compartment apparatus, such as the one described and used in this work, appears to be an appropriate and promising means of assessing the effectiveness of an FML to contain a given leachate.

TABLE 41. COMPATIBILITY TESTING OF HDPE FML IN SPIKED DEIONIZED WATER[a]

60-Mil HDPE FML[b]--Unexposed and After One, Two, Three, and Four Months of Exposure at 23°C in Tank III

Property	Average initial values	Exposure time, months 1	2	3	4
Physical properties		Percent retention[c]			
Tensile at yield	2635 psi	103	102	106	106
Elongation at yield	19%	79	79	69	77
Tensile at break	4060 psi	100	107	112	110
Elongation at break	795%	102	107	106	107
Stress at 100% elongation	1815 psi	99	100	102	101
Stress at 200% elongation	1875 psi	98	98	101	99
Modulus of elasticity[d]	114,750 psi	104	100	108	117
Tear strength	790 ppi	99	101	99	101
Puncture resistance	151[e] lb	97	98	95	100
Hydrostatic resistance	861[e] psi	101	97	98	118
		Change in points			
Hardness, Duro D 5-second reading	60	-2	-2	-2	-2

[a] The immersion liquid was deionized water spiked with a mixture of the following: TCA, TCE, benzene, toluene, o-, m-, and p-xylenes, acetone, MEK, di(ethylhexyl) phthalate, and tri-n-butyl phosphate.

[b] Matrecon identification number 392.

[c] Average percent retention determined from values in both machine and transverse direction of test.

[d] Measured using 0.5 x 8-in. strip specimens with an initial jaw separation of 4.0 in. and an initial strain rate of 0.1 in./in. min. Using a specimen with a 10-in. gage length as specified in ASTM D882-83 would result in higher values.

[e] Normalized for 100-mil thickness.

TABLE 42. COMPATIBILITY TESTING OF HDPE FML IN SPIKED DEIONIZED WATER[a]

60-Mil HDPE FML[b]--Unexposed and After One, Two, Three, and Four Months of Exposure at 50°C in Tank II

Property	Average initial values	Exposure time, months 1	2	3	4
Physical properties		Percent retention[c]			
Tensile at yield	2635 psi	106	108	108	108
Elongation at yield	19%	89	79	84	79
Tensile at break	4060 psi	111	112	103	108
Elongation at break	795%	107	106	95	105
Stress at 100% elongation	1815 psi	103	105	105	103
Stress at 200% elongation	1875 psi	102	103	104	102
Modulus of elasticity[d]	114,750 psi	91	92	105	103
Tear strength	790 ppi	102	104	104	103
Puncture resistance	151[e] lb	101	103	101	103
Hydrostatic resistance	861[e] psi	102	102	111	104
		Change in points			
Hardness, Duro D 5-second reading	60	-2	-1	-2	-1

[a] The immersion liquid was deionized water spiked with a mixture of the following: TCA, TCE, benzene, toluene, o-, m-, and p-xylenes, acetone, MEK, di(ethylhexyl) phthalate, and tri-n-butyl phosphate.

[b] Matrecon identification number 392.

[c] Average percent retention determined from values in both machine and transverse direction of test.

[d] Measured using 0.5 x 8-in. strip specimens with an initial jaw separation of 4.0 in. and an initial strain rate of 0.1 in./in. min. Using a specimen with a 10-in. gage length as specified in ASTM D882-83 would result in higher values.

[e] Normalized for 100-mil thickness.

TABLE 43. COMPATIBILITY TESTING OF HDPE FML IN SPIKED DEIONIZED WATER[a]

60-Mil HDPE FML[b]--Unexposed and After One, Two, Three, and Four Months of Exposure at 50°C in Tank IV

Property	Average initial values	Exposure time, months 1	2	3	4
Physical properties		Percent retention[c]			
Tensile at yield	2635 psi	107	104	104	110
Elongation at yield	19%	82	82	98	77
Tensile at break	4060 psi	98	107	101	109
Elongation at break	795%	100	106	102	106
Stress at 100% elongation	1815 psi	103	100	101	104
Stress at 200% elongation	1875 psi	101	99	100	101
Modulus of elasticity[d]	114,750 psi	94	98	109	113
Tear strength	790 ppi	101	104	100	104
Puncture resistance	151[e] lb	99	103	99	102
Hydrostatic resistance	861[e] psi	104	100	101	105
		Change in points			
Hardness, Duro D 5-second reading	60	-3	-1	-2	-2

[a] The immersion liquid was deionized water spiked with a mixture of the following: TCA, TCE, benzene, toluene, o-, m-, and p-xylenes, acetone, MEK, di(ethylhexyl) phthalate, and tri-n-butyl phosphate.

[b] Matrecon identification number 392.

[c] Average percent retention determined from values in both machine and transverse direction of test.

[d] Measured using 0.5 x 8-in. strip specimens with an initial jaw separation of 4.0 in. and an initial strain rate of 0.1 in./in. min. Using a specimen with a 10-in. gage length as specified in ASTM D882-83 would result in higher values.

[e] Normalized for 100-mil thickness.

TABLE 44. GC ANALYSIS OF THE EXPOSED FML SAMPLES

Exposure temperature, tank number, and time	Volatiles in FML by HSGC, mg/g									GC of extractables, mg/g		
	Acetone (197[a])	MEK (201[a])	1,1,1-TCA (326[a])	Benzene (231[a])	TCE (406[a])	Toluene (338[a])	m- and p-Xylenes (191[a])	o-Xylene (103[a])	Total	TBP (251[a])	DEHP (250[a])	Total
Tank I (23°C)												
34 days	0	0	1.42	0.46	1.58	2.63	1.86	1.17	8.72	0.32	0.11	0.43
69 days	0	0	0.45	0.18	0.98	1.75	4.17	1.53	9.06	5.62	0.41	6.03
105 days	0	0	0.25	0.04	0.21	0.34	1.85	0.82	3.51	6.44	0.63	7.07
139 days	0	0	0	0	0	0.02	0.19	0.04	0.25	...	...	...
Tank III (23°C)												
34 days	0	0	0.68	0.30	1.26	2.25	1.33	0.80	6.62	0.08	0.08	0.16
69 days	0	0	0.18	0.05	0.30	0.81	3.00	1.03	5.37	0.52	0.14	0.66
105 days	0	0	0.08	0.01	0.07	0.16	1.26	0.53	2.11	5.29	0.32	5.61
139 days	0	0	0.02	0.00	0.01	0.05	0.08	0.00	0.16	...	...	...
Tank II (50°C)												
34 days	0	0	0.1	0.02	0.16	0.66	0.78	0.57	2.29	1.61	0.31	1.92
69 days	0	0	0.01	0	0.08	0.05	1.06	0.46	1.66	3.34	0.42	3.76
105 days	0	0	0	0	0	0	0.17	0.14	0.31	9.47	0.64	10.11
139 days	0	0	0	0	0	0	0	0	0	...	...	...
Tank IV (50°C)												
34 days	0	0	0.10	0.11	0.40	0.96	1.29	0.83	3.69	1.53	0.26	1.79
69 days	0	0	0	0.01	1.01	0.03	0.82	0.37	2.40	5.31	0.42	5.73
105 days	0	0	0	0	0	0	0.10	0.11	0.21	7.57	0.52	8.09
139 days	0	0	0	0	0	0	0	0	0	...	...	...

[a] Total concentration in (mg/L) of the organics injected in the water in two portions. Value assumes complete dissolution in the water.

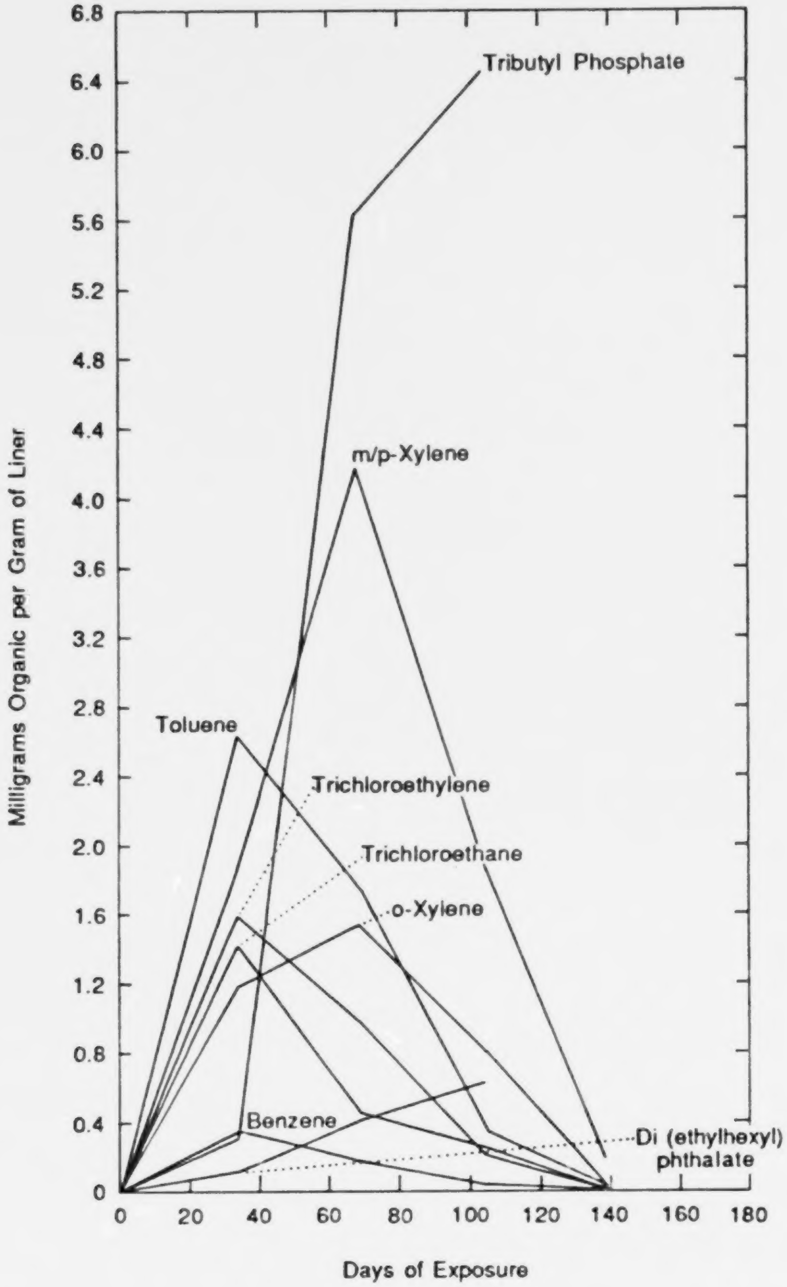

Figure 16. Concentration as a function of time of absorbed organics in exposed HDPE FMLs recovered from Tank I (23°C). The last addition of the organics was at the beginning of the second exposure period.

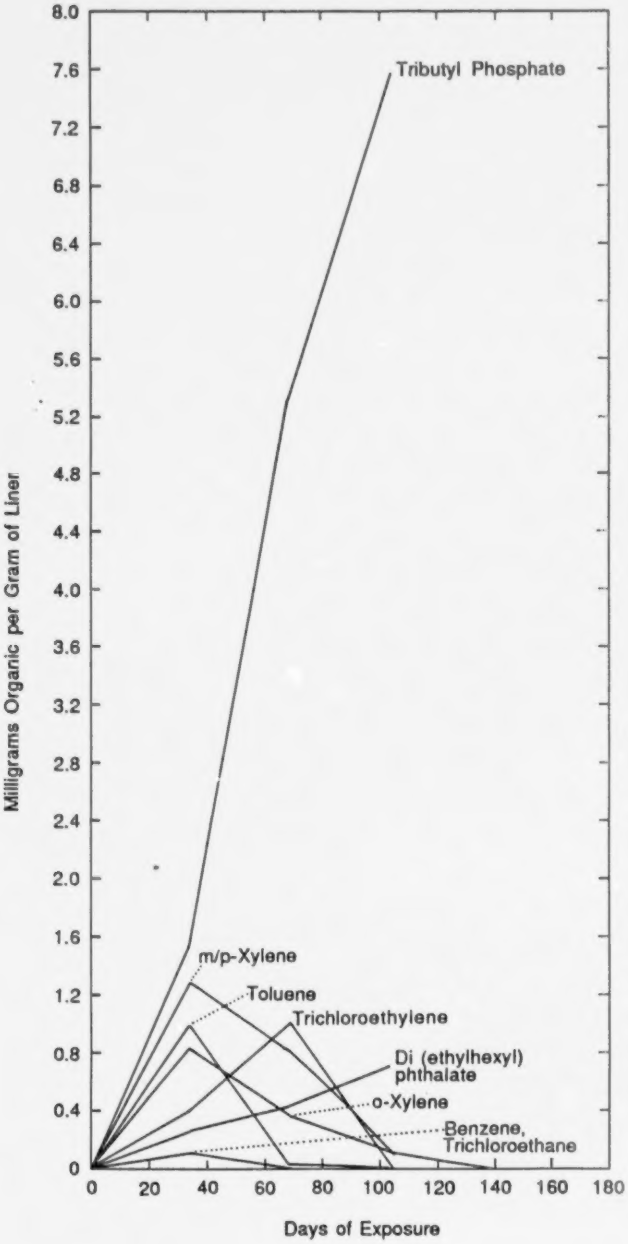

Figure 17. Concentration as a function of time of absorbed organics in exposed HDPE FMLs recovered from Tank IV (50°C). The last addition of the organics was at the beginning of the second exposure period.

TABLE 45. SUMMARY OF ANALYTICAL TESTS OF EXPOSED FML SAMPLES

Exposure temperature, tank number, and time	Weight change, %	Volatiles, %	Extractables, %
Tank I (23°C)			
34 days	+1.2	1.31	0.74
66 days	+1.3	1.19	0.80
105 days	+1.9	0.99	0.83
139 days	+1.6	0.70	1.13
Tank III (23°C)			
34 days	+1.3	0.67	0.84
66 days	+0.9	0.48	0.82
105 days	+1.8	0.37	1.47
139 days	+1.5	0.24	1.71
Tank II (50°C)			
34 days	+0.8	0.97	1.42
66 days	+1.0	0.85	1.28
105 days	+1.5	0.58	0.65
139 days	+0.5	0.33	1.42
Tank IV (50°C)			
34 days	+1.1	0.80	0.55
66 days	+0.7	0.37	0.87
105 days	+0.9	0.22	0.84
139 days	+0.9	0.22	1.57
Unexposed FML			
0 day	...	0.09	0.65

No failure occurred in any of the specimens due to environmental stress-cracking during the four months of immersion in the test liquid at either 23° or 50°C.

There were few differences in the results of physical testing between the samples exposed at the same temperature, as well as at different temperatures, thus indicating that this type of test is replicable. The similarity of the results at the two tempertures indicates that within the 23° to 50°C range, temperature does not have a significant effect on the HDPE samples in this particular synthetic leachate.

TABLE 46. WEIGHT CHANGE OF THE DISK SPECIMENS[a] DURING EXPOSURE TO THE SPIKED DEIONIZED WATER[b]

Exposure temperature and tank number	Weight change, %	
	One-month	Two-months
23°C - Tank I	+1.0	+1.0
23°C - Tank III	+0.6	+0.7
50°C - Tank II	+0.6	-1.8
50°C - Tank IV	+0.6	-2.6

[a] Two-inch-diameter circular specimens die-cut from 60-mil HDPE.

[b] The disk specimens were placed in the exposure cells at the beginning of the third month of exposure for the slab samples.

The leachate appeared to have little effect on the FML; consequently, the FML appears to be compatible with the synthetic leachate, at least to the low concentrations of organics and plasticizers present in the DI water. It is likely that the loss of volatiles during the test was the principal factor in the small effect that was observed on the FMLs. Replacing the test liquid with another portion of the same initial concentration of organics should maintain the concentration of the organics.

Discussion and Conclusions

The test data on the volatiles and weight changes indicate that there were significant losses in volatiles from the tanks and from the FMLs as the test proceeded. These losses are reflected in the physical test data by the small changes in the values of properties. The GC analyses showed that the concentrations of all of the volatile organics dropped, both in the exposed FMLs and in the water, indicating a relationship between the concentration of the organics in the water and in the FML. As indicated by the increase in extractables, the two plasticizers that were incorporated in the original test liquid were gradually absorbed by the FML samples. This conclusion was confirmed by the results of the GC analyses. The increase in extractables, however, did not affect the physical properties of the exposed samples. The results of the previous 9090 test performed for this project indicated that an increase in volatiles content can affect the physical properties of an HDPE FML. The net result indicated the importance of volatile organics in affecting the properties of a polymeric FML.

It is concluded from the results of this experiment that tight control of volatiles in an EPA Method 9090 test is essential, and that the concentration of all constituents in a leachate used in a compatibility test must be maintained at original levels.

The data indicate that "synthetic leachates" require more development in order to be used in liner/waste compatibility testing. It appears that addition of a spiking of a few volatile organics to water to yield a "leachate" is not sufficient and that a broader background of organics is needed. It should be noted that, in the test using spiked leachate, the volatile organics in the spike plus organics in the original leachate had greater effects on the properties of an FML than did essentially the same volatile organics alone when added in the spike.

The loss of volatiles at the higher exposure temperature resulted in higher retention of properties than at the lower exposure temperature, probably a result of the evaporation of volatile organics. These results indicate problems in performing the 9090 test at 50°C and higher.

EVAPORATION OF VOLATILE ORGANICS FROM WATER SOLUTIONS AND EXPOSED FMLS

Introduction

In actual service in a waste storage or disposal facility the liquid that may contact a liner is generally a dilute solution of water and various dissolved constituents, some of which are inorganic and others organic; the latter can be either volatile or nonvolatile, or both. The concentrations of the constituents will probably be low and more or less constant, or will change only slowly with time. In performing laboratory testing of an FML to assess its compatibility with a waste liquid, it is desirable to simulate as much as possible the conditions that exist in service. Inasmuch as the amounts of organics that are absorbed by an FML affects its properties, the concentrations of the organics must remain essentially constant. As the volatile components can evaporate relatively easily, FML samples that are being recovered and tested should be protected from loss of volatiles. A loss of volatiles can result in values for many properties different from values for the properties of the liner as it existed at the time it was removed from service.

The effects of exposing an FML to a service environment can be of one or more of three basic types:

- Degradation of the polymer itself, either by reduction in molecular weight or by crosslinking, either of which could cause drastic changes in properties.

- Extraction of plasticizers or other compounding ingredients in the FML. This can result in a variety of effects including hardening and loss of antioxidants and other antidegradants which could result in faster rates of degradation of the polymer.

- Swelling of the FML due to absorption of organics and water. In this case, exposure may result in loss of physical properties and increases in permeability. The evaporation of volatile absorbed constituents may result in recovery of many of the baseline values of the FML; consequently, the effects of the exposure that would be measured at the time a sample is removed from service are lost. It would be ideal if the testing of an FML specimen could be performed while it is immersed in a waste stream as is sometimes done in the testing of the compatibility of rubbers and plastic compositions with various solvents, oils, and other fluids.

It is the third factor which is of particular concern in the testing of FMLs that have been in contact with waste liquids that contain minor amounts of organics. To demonstrate some of the effects resulting from the evaporation of volatiles, either from the test tank in which the FMLs are being exposed in an EPA 9090-type test or from the loss of volatiles after removal from immersion, several experiments were performed; these are described in the following subsections.

Evaporation of Volatile Organics from Aqueous Solutions

The evaporation of several volatile organics from dilute aqueous solutions was measured. These measurements were made by preparing solutions of various types of organics in concentrations of 200 to 10,000 mg/L in 400 mL beakers that were half filled. The beakers were left uncovered and the organics were allowed to evaporate. The concentrations of the organics remaining in the beaker was monitored by GC analysis. The results are presented in Figures 18 through 21. The data in these figures show a pronounced loss from the solutions for all of the organics, particularly the aromatic hydrocarbons toluene and xylene. The comparative rates of loss are illustrated in Table 47, in which the times to one-half of the initial concentrations are presented.

These results indicate the need when conducting compatibility tests to take precautions to prevent the loss of volatiles from the time a waste liquid is received for test through the four months of exposure. These data also indicate the need to prevent loss of the volatiles from the time the waste liquid is collected through shipping and testing. The results confirm the data that were obtained in the two EPA Method 9090-type tests which are described above.

Evaporation of Organics from Saturated FML Specimens

The loss of volatiles from exposed FML samples was demonstrated in a series of tests with polyethylene and various organics. Typical results are shown in Figure 22 for toluene, TCE, and a mixture of organics that were absorbed by small samples of a 100-mil HDPE FML. Again, there was rapid evaporation of the volatile constituents when a sample was withdrawn from the organic. The evaporation of a volatile organic from an FML exposed to volatiles is generally not as rapid as the evaporation from an aqueous solution; however, in performing a compatibility test, even though the time is relatively short between removal of an FML sample from the waste and the testing, these data demonstrate the need for protecting the samples once they are withdrawn from a waste liquid containing volatile organics. It is recognized that the rate of evaporation of a volatile organic or water from an FML sample is affected by the type of organic, the test temperature, air movement, and sample size, thickness, and shape. It should be pointed out that even during the actual physical testing, such as tensile testing, the specimen loses volatiles. This loss may be a factor due to the duration of the test and the increased surface and reduced thickness of the specimen during the actual physical testing.

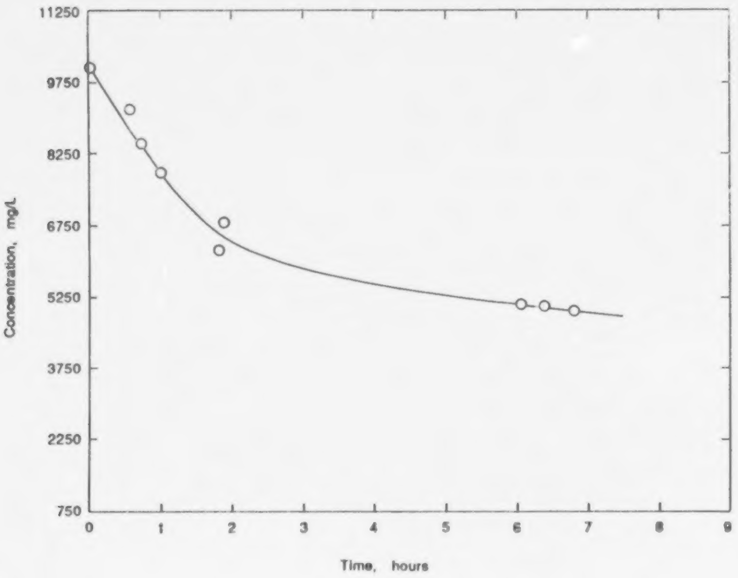

Figure 18. Reduction in concentration of acetone in a dilute aqueous solution of initial concentration of 10,000 mg/L (1%) by evaporation from an open beaker at room temperature. 200 mL of solution was in a 400 mL beaker.

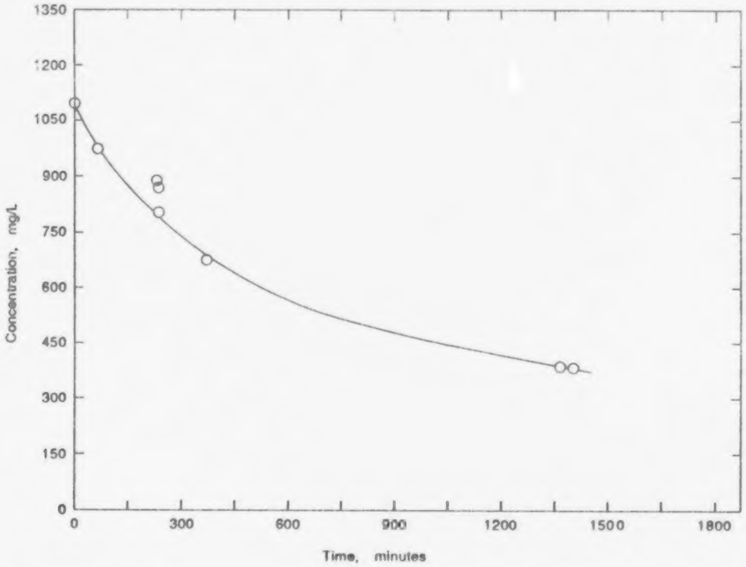

Figure 19. Reduction in concentration of TCE in a dilute aqueous solution of initial concentration of 1,100 mg/L by evaporation from an open beaker at room temperature. 200 mL of solution was in a 400 mL beaker.

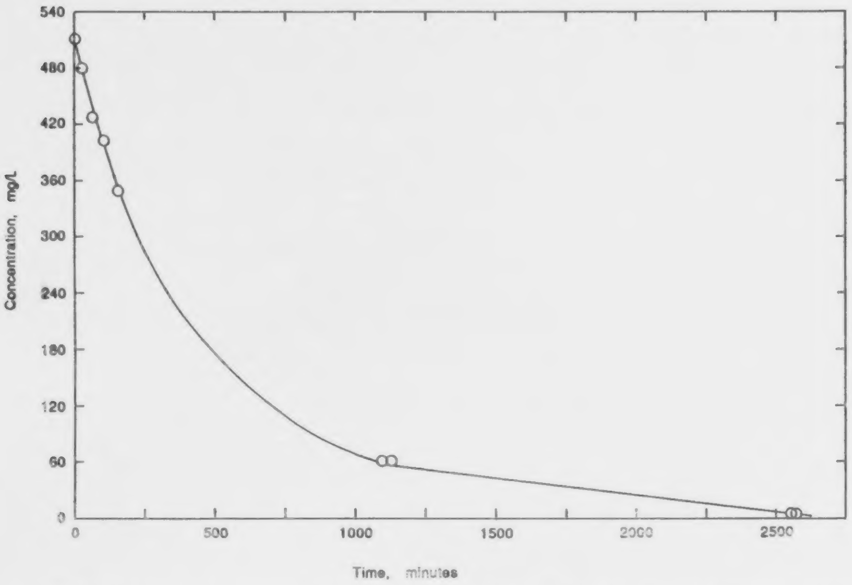

Figure 20. Reduction in concentration of toluene in a dilute aqueous solution of initial concentration of 520 mg/L by evaporation from an open beaker at room temperature. 200 mL of solution was in a 400 mL beaker.

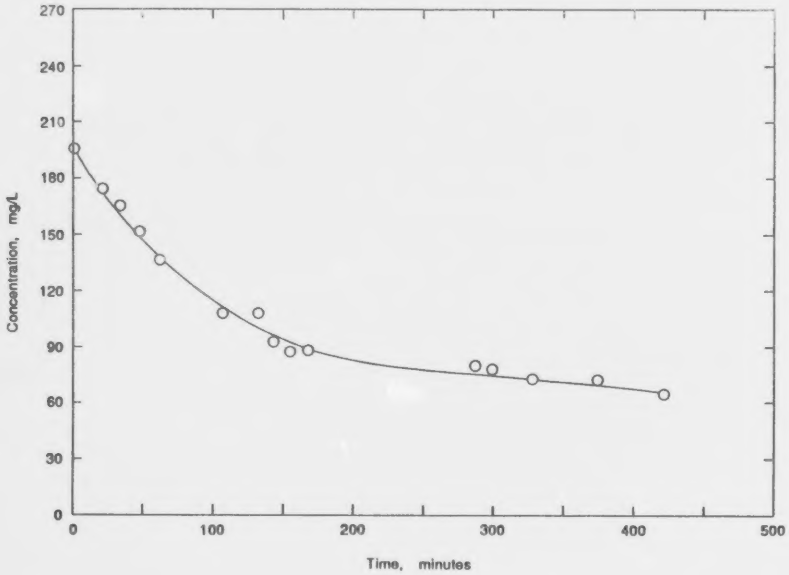

Figure 21. Reduction in concentration of m-xylene in a dilute aqueous solution of initial concentration of 195 mg/L (saturated) by evaporation from an open beaker at room temperature. 200 mL of solution was in a 400 mL beaker.

TABLE 47. EVAPORATION OF VOLATILE ORGANICS FROM AQUEOUS SOLUTIONS

Organic	Initial concentration, mg/L	Time to one-half initial concentration, min.
Acetone	10,000	384
Trichloroethylene	1,100	650
Toluene	520	310
m-Xylene	195	138

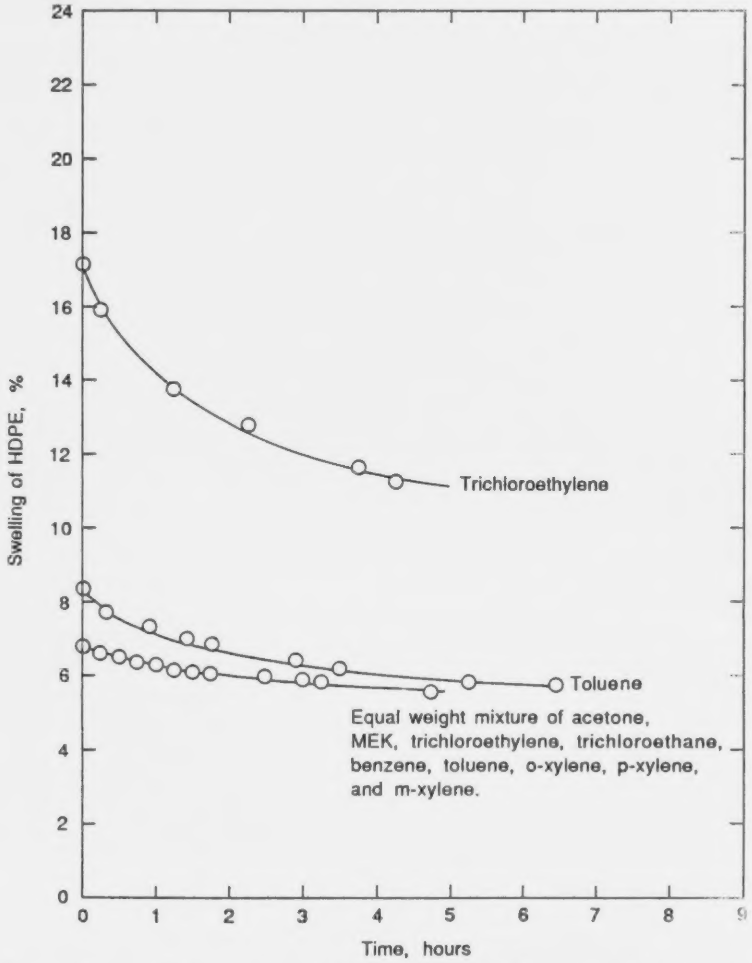

Figure 22. Loss of organics from HDPE FML samples saturated with different organics.

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APPENDIX A

ORGANICS USED IN FML SOLUBILITY PARAMETER STUDY AND SELECTED PROPERTIES

Name	δ[a], cal$^{1/2}$ cm$^{-3/2}$				Organic, no., and code[b]				Property			
	o	d	p	h	No.	R_d	R_p	R_h	MP[c], °C	BP[c], °C	Density[c], g/cm^3	Solubility in water[d] at 25°C, mg/L
n-Octane	7.6	7.6	0	0	1	1	1	1	-57	125	0.703	0.66
Isoamyl acetate	8.4	7.5	1.5	3.4	2	1	1	2	-78	142	0.876	20,000
2-Ethyl-1-hexanol	9.9	7.8	1.6	5.8	3	1	1	3	-76	183	0.833	700 (20°C)
Methyl isobutyl ketone	8.3	7.5	3.0	2.0	4	1	2	1	-80	114	0.801	17,000
Ethyl acetate	8.9	7.7	2.6	3.5	5	1	2	2	-84	77	0.902	80,800
n-Propanol	12.0	7.8	3.3	8.5	6	1	2	3	-127	97	0.804	Miscible
Nitroethane	11.1	7.8	7.6	2.2	7	1	3	1	-90	112	1.045	46,800
Methyl ethyl ketone	9.3	7.8	4.4	2.5	8	1	3	2	-87	80	0.805	240,000
Methanol	14.5	7.4	6.0	10.9	9	1	3	3	-98	65	0.791	Miscible
Cyclohexane	8.2	8.2	0.0	0.1	10	2	1	1	6.5	81	0.779	55
Diethyl carbonate	8.8	8.1	1.5	3.0	11	2	1	2	-43	126	0.975	Insoluble
Cyclohexanol	10.9	8.5	2.0	6.6	12	2	1	3	22	160	0.963	37,500 (26.5°C)
Di(ethylhexyl) phthalate	8.9	8.1	3.4	1.5	13	2	2	1	-50	384	0.981	0.4[e]
Cyclohexanone	9.6	8.7	3.1	2.5	14	2	2	2	-47	155	0.947	23,000
Furfuryl alcohol	11.9	8.5	3.7	7.4	15	2	2	3	-29	170	1.135	Miscible
Diethyl phthalate	10.0	8.6	4.7	2.2	16	2	3	1	-3	298	1.118	0.09[e]
N,N-Dimethylacetamide	11.1	8.2	5.6	5.0	17	2	3	2	-20	165	0.937	Miscible
Ethylene glycol	16.1	8.3	5.4	12.7	18	2	3	3	-13	196	1.113	Miscible
Tetralin	9.8	9.6	1.0	1.4	19	3	1	1	-35	207	0.973	Insoluble
Trichloroethylene	9.3	8.8	1.5	2.6	20	3	1	2	-87	87	1.462	1,100
m-Cresol	11.1	8.8	2.5	6.3	21	3	1	3	10	203	1.034	25,100 (40°C)
Tetrachloroethylene	9.9	9.3	3.2	1.4	22	3	2	1	-22	121	1.623	2,870 (20°C)
Quinoline	10.8	9.5	3.4	3.7	23	3	2	2	-15	237	1.095	6,090 (20°C)
Benzyl alcohol	11.6	9.0	3.1	6.7	24	3	2	3	-15	205	1.045	800 (20°C)
Propylene carbonate	13.3	9.8	8.8	2.0	25	3	3	1	-55	240	1.189	Moderate
Butyrolactone	12.9	9.3	8.1	3.6	26	3	3	2	-45	204	1.12	Miscible
2-Pyrrolidone	13.9	9.5	8.5	5.5	27	3	3	3	25	245	1.12	Miscible
Water	23.4	7.6	7.8	20.7	28	1	3	3	0	100	1.00	...
Isooctane	7.0	7.0	0	0	29	1	1	1	-107	99	0.692	2.4
Xylenes (o, m, and p)	8.8	8.7	0.5	1.5	30	2	1	1	-48-+13	138-144	0.868	190
Acetone	9.8	7.6	5.1	3.4	31	1	3	2	-95	56	0.791	Miscible

[a] Barton (1975). δ_o = Hildebrand solubility parameter; δ_d = dispersive solubility parameter; δ_p = polarity solubility parameter; and δ_h = hydrogen-bonding solubility parameter.

[b] Each code was made up of three digits representing the range values assigned to an organic after the ordering of organics by each component solubility parameter as presented in Section 5. R_d is the range value for the dispersive solubility parameter; R_p the range value for the polarity solubility parameter; and R_h the range value for the hydrogen-bonding solubility parameter. Each selected test organic was assigned a unique number.

[c] Lange (1967); MP is the melting point and BP is the boiling point of the organic.

[d] Riddick and Bunger (1970).

[e] EPA (1982).

APPENDIX B

PHYSICAL AND ANALYTICAL PROPERTIES OF THE COMMERCIALLY MANUFACTURED POLYMERIC SHEETINGS

This appendix presents the results of measuring selected physical and analytical properties of the commercially manufactured polymeric sheeting used in this research project. Table B-1 presents, by the type of sheeting, the methods used in the physical and analytical testing. The solvents used to extract the polymeric sheetings are presented in Table B-2. The composition of the laboratory-prepared compounds that were included in this study are presented in Tables B-3 and B-4. These compounds include four CSPE compositions, a nitrile rubber composition, and a PVC composition plasticized with Di(ethylhexyl) phthalate. Among the four CSPE compositions are three gum compounds that contain no filler but vary in the level of crosslinking. The fourth CSPE composition contains 100 parts of carbon black similar to that used in CSPE liner compounds. Table B-5 presents details on the procedures used in the tensile and tear resistance testing.

It should be noted that some of this testing was performed in conjunction with various exposure tests which require the testing of limited size samples after exposure to a waste test liquid. Thus, the methods cited for determining tensile properties and modulus elasticity were modified to allow for the testing of specimens smaller than those required in the respective methods. Details are presented in Tables B-1 and B-5 and in Figure B-1.

The results of the testing are presented in Tables B-6 through B-9.

REFERENCES

Annual Book of ASTM Standards. Issued annually in several parts. American Society for Testing and Materials, Philadelphia, PA:

- D297-81, "Methods for Rubber Products - Chemical Analysis."
- D412-83, "Test Methods for Rubber Properties in Tension."
- D624-86, "Test Method for Rubber Property - Tear Resistance."
- D638-84, "Test Method for Tensile Properties of Plastics."
- D751-79, "Method of Testing Coated Fabrics."

TABLE B-1. TEST METHODS[a] USED TO DETERMINE PHYSICAL AND ANALYTICAL PROPERTIES OF POLYMERIC SHEETINGS

	Sheeting without fabric reinforcement			
Property	Thermoplastic	Crosslinked	Semicrystalline	Fabric reinforced
Analytical properties				
Volatiles	MTM-1[b]	MTM-1[b]	MTM-1[b]	MTM-1[b]
Extractables	MTM-2[c]	MTM-2[c]	MTM-2[c]	MTM-2[c]
Ash	ASTM D297, Section 34	ASTM D297, Section 34	ASTM D297, Section 34	ASTM D297, Section 34
Specific gravity	ASTM D792, Method A	ASTM D297, Method A	ASTM D792, Method A	ASTM D792, Method A
Physical properties				
Thickness (average)	ASTM D638[d]	ASTM D412[d]	ASTM D638[d]	ASTM D751, Section 6[d]
Tensile properties[e]	ASTM D638	ASTM D412	ASTM D638 (modified)[e]	ASTM D751, Method B
Tear resistance[e]	ASTM D1004 (modified)[e]	ASTM D624, Die C	ASTM D1004	ASTM D751, Tongue Method (8 x 8-in. test specimen)[e]
Modulus of elasticity	na	na	ASTM D882, Method A (modified)[f]	na
Hardness (Duormeter A or D)	ASTM D2240	ASTM D2240	ASTM D2240	ASTM D2240
Puncture resistance	FTMS 101C, Method 2065	FTMS 101C, Method 2065	FTMS 101C, Method 2065	FTMS 101C, Method 2065

[a] See references of this appendix for the sources and titles of the test methods.

[b] Matrecon Test Method-1 (Matrecon, 1983, pp 338-39).

[c] Matrecon Test Method-2 (Matrecon, 1983, pp 340-43). Solvents used to extract polymeric sheetings are presented in Table B-2.

[d] Reported thickness values are the averages of all the values measured on test specimens used in the physical property testing.

[e] Details of tensile and tear resistance testing are presented in Table B-5.

[f] Measured using 0.5 x 6-in. strip specimens with an initial jaw separation of 2.0 in. at the standard strain rate of 0.1 in./in. min. Using a specimen size large enough so that specimens would be tested with an initial jaw separation of 10.0 in. as specified by ASTM D882-83 would result in higher values.

na = not applicable.

TABLE B-2. SOLVENTS USED FOR EXTRACTION OF POLYMERIC SHEETINGS

Polymer	Extraction solvent
Chlorinated polyethylene (CPE)	n-Heptane
Chlorosulfonated polyethylene (CSPE)	Acetone
Epichlorohydrin rubber (ECO)	Methyl ethyl ketone
Ethylene propylene rubber (EPDM)	Methyl ethyl ketone
Ethylene vinyl acetate (EVA)	Ethyl alcohol
Neoprene (CR)	Acetone
Polybutylene (PB)	Methyl ethyl ketone
Polyester elastomer (PEL)	n-Heptane
Polyethylene:	
Low-density (LDPE)	Methyl ethyl ketone
Linear low-density (LLDPE)	Methyl ethyl ketone
High-density (HDPE)	Methyl ethyl ketone
HDPE/EPDM-alloy (HDPE-A)	Methyl ethyl ketone
Polyurethane (PU)	n-Heptane
Polyvinyl chloride (PVC)	2:1 blend of carbon tetrachloride and methyl alcohol
Elasticized polyvinyl chloride (PVC-E)	Methyl alcohol
Polyvinyl chloride--oil-resistant (PVC-OR)	2:1 blend of carbon tetrachloride and methyl alcohol

TABLE B-3. COMPOSITION OF LABORATORY-PREPARED COMPOUNDS OF CSPE, NITRILE RUBBER, AND POLYVINYL CHLORIDE[a]

Ingredient	CSPE				Nitrile rubber	PVC
	DOY-3[b]	DOZ-2[b]	DPO[b]	DPP[b]	DPN[b]	DPO[b]
CSPE (Hypalon 45)	100	100	100	100	...	...
Nitrile rubber (Hycar 1052-30)	...	...	...	...	100	...
PVC (Geon 135)	...	...	...	...	...	100
Di(ethylhexyl) phthalate	...	...	...	...	...	50
MT black	...	100	...	...	...	...
MgO (Maglite D)	4	4	10	4	...	...
Peroxide (Varox powder)	...	...	6	1.5	...	...
HVA-2[c]	...	...	2	0.5	...	...
Lead stearate	...	...	...	...	...	2.0
Stearic acid (F300)	...	...	...	...	1.0	0.2
ZnO (Protox 168)	...	...	...	...	5.0	...
TMTDS[d] (Tuex)	...	...	...	...	3.5	...
Carbowax 4000	1.5	1.5	...	...	...	...
Pentaerythritol	3.0	...	...	...	...	...
Tetrone A[e]	2.0	...	...	...	...	...
Total	110.5	205.5	118.0	106.0	109.5	152.2

[a] Formulation in parts by weight.

[b] Matrecon identification code.

[c] HVA-2 = N,N-m-phenylenedimaleimide (DuPont), a curing adjuvant for CSPE.

[d] TMTDS = tetramethyl thiuram disulfide.

[e] Tetrone A = dipentamethylene thiuram hexasulfide, accelerator or sulfur source.

TABLE B-4. MOLDING CONDITIONS AND EXTRACTABLES OF THE LABORATORY-PREPARED COMPOUNDS

Item	CSPE				Nitrile rubber	PVC
	DOY-3[a]	DOZ-2[a]	DPO[a]	DPP[a]	DPN[a]	DPQ[a]
Molding conditions[b]						
Temperature, °C	160	160	150	140	150	150
Time, min.	25	60	20	40[c]	40	[d]
Extractables[e], %	5.9	<1.0	6.8	1.9	1.0	34.3

[a] Matrecon identification number.

[b] Molded in small slabs of 25 to 30-mil thickness.

[c] Cooled in the press.

[d] Cooled immediately after filled mold was placed in a press.

[e] Extractables of the composition were calculated based upon their respective formulations. The polymer component was assumed to be nonextractable.

TABLE B-5. DETAILS OF TENSILE AND TEAR RESISTANCE TEST METHODS USED IN TESTING

Test and test conditions	Sheeting without fabric reinforcement			Sheeting with fabric reinforcement
	Crosslinked	Thermoplastic	Semicrystalline	
Tensile properties				
Method	ASTM D412	ASTM D638	ASTM D638	ASTM D751, Method B
Type of specimen	"Special" dumbbell[a]	"Special" dumbbell[a]	ASTM D638 Type IV dumbbell	1-in. wide strip and 2-in. jaw separation
Jaw separation rate	20 ipm[b]	20 ipm[b]	2 ipm[b]	12 ipm[b]
Tear resistance				
Method	ASTM D624	ASTM D1004	ASTM D1004	ASTM D751, Tongue Method
Type of specimen	Die C	Die C[c]	Die C[c]	8 x 8-in. test specimen[d]
Speed of test	20 ipm[b]	20 ipm[b]	2 ipm[b]	12 ipm[b]

[a] See Figure B-1.

[b] ipm = inches per minute.

[c] Required test specimen is the same as Die C from ASTM D624.

[d] National Sanitation Foundation, 1985, p A-4.

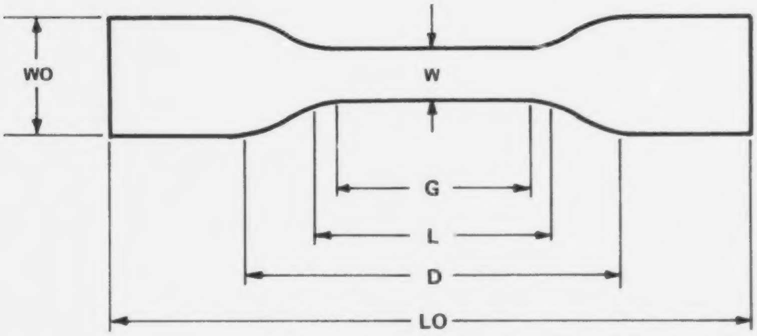

Figure B-1. Die for "special" dumbbell used in tensile testing of the crosslinked and thermoplastic sheetings. Dimensions are as follows:

W	- Width of narrow section	0.25 in.
L	- Length of narrow section	1.25 in.
WO	- Width overall	0.625 in.
LO	- Length overall	3.50 in.
G	- Gage length	1.00 in.
D	- Distance between grips	2.00 in.

The width of the narrow section of this specimen, W, is the same as that of the ASTM D412 Die C dumbbell and the ASTM D638 Type IV dumbbell. It should be noted that these two dumbbells esentially have the same dimensions. The length of the narrow section, L, and the overall length, LO, of the ASTM D412 Die C/ ASTM D638 Type IV dumbbell are, respectively, 1.30 in. and 4.50 inches.

TABLE B-6. ANALYTICAL AND PHYSICAL PROPERTIES OF CHLORINATED POLYETHYLENE, CHLOROSULFONATED POLYETHYLENE, AND EPICHLOROHYDRIN RUBBER SHEETING

Polymer[a]		CPE	CPE	CPE	CSPE	CSPE	ECO
Liner number[b]		195	335R	378R	169R	174R	178
Nominal thickness, mil		30	40	...	30	36	60
Type of compound[c]		TP/AM	TP/AM	TP/AM	TP/AM	TP/AM	XL/AM
Thread count, epi[d]		na	9x9	9x9	8x8	10x10	na
	Direction of test						
Analytical Properties:							
Specific gravity		1.26	1.312	1.333	1.297	1.364	1.458
Ash-db, %		...	15.98	...	2.77	27.37	4.50
Volatiles, %		0.12	0.40	0.25	0.39	0.15	0.55
Extractables-db, %		14.85	4.48	7.94	11.29	7.15	7.36[e]
Physical properties:							
Average thickness, mil		30.8	39.8	35.0	27.9	37.7	66.9
Tensile of fabric at break, ppi	Machine	...	134.3	194.4	33.0	190.0	...
	Transverse	...	133.6	164.4	31.7	185.0	...
Elongation of fabric at break, %	Machine	...	31	29	25	24	...
	Transverse	...	30	32	26	32	...
Tensile at break, psi	Machine	1575	...	...	...	...	1050
	Transverse	1405	...	...	...	...	1120
Tensile at break, ppi	Machine	48.4	39.8	51.0	31.8	33.4	70.5
	Transverse	43.2	26.3	164.0	30.9	30.0	76.1
Elongation at break, %	Machine	315	570	39	275	125	215
	Transverse	440	340	32	285	155	200
Stress at 100% elongation, psi	Machine	1110	...	...	...	...	685
	Transverse	585	...	...	...	...	775
Stress at 100% elongation, ppi	Machine	34.0	29.7	...	23.9	32.5	46.0
	Transverse	18.0	20.3	...	22.4	28.1	52.6
Stress at 200% elongation, psi	Machine	1295	...	...	...	...	1035
	Transverse	760	...	...	...	...	1120
Stress at 200% elongation, ppi	Machine	39.8	31.2	...	30.9	...	69.6
	Transverse	23.3	23.5	...	29.3	...	76.2
Tear strength-tongue, lb	Machine	...	...	83.1[f]	15.4	142.0	...
	Transverse	...	...	78.4[f]	28.6	107.0	...
Tear strength-Die C, ppi	Machine	268	...	...	...	...	162
	Transverse	215	...	...	...	...	165
Puncture resistance:							
Thickness, mil		31.0	39.6	...	29.0	37.6	67.2
Maximum stress-avg., lb		38.1	50.7	...	27.2	68.0	40.0
Elongation, in.		0.86	0.31	...	0.67	0.30	0.68
Hardness, Durometer points		82A	69A	79A	85A	67A	64A
Hardness, Durometer points		28D	...	...	34D	...	...

[a] CPE = chlorinated polyethylene; CSPE = chlorosulfonated polyethylene; ECO = epichlorohydrin rubber.

[b] Serial number assigned by Matrecon to each lot of sheeting received; R = fabric-reinforced sheeting.

[c] TP = thermoplastic; AM = amorphous; XL = crosslinked.

[d] epi = ends per inch.

[e] With methyl ethyl ketone.

[f] Maximum peak values obtained before delamination and tearing in the opposite direction occurred.

TABLE B-7. ANALYTICAL AND PHYSICAL PROPERTIES OF ETHYLENE PROPYLENE RUBBER, ETHYLENE VINYL ACETATE, NEOPRENE, POLYBUTYLENE, AND POLYESTER ELASTOMER SHEETING

Polymer[a]		EPDM	EVA	Neoprene	PB	PEL	PEL
Liner number[b]		232	308A	168	221A	316	323
Nominal thickness, mil		60	20	33	30	20	20
Type of compound[c]		XL/AM	TP/AM	XL/AM	CX	TP/CX/AM	TP/CX/AM
	Direction of test						
Analytical Properties:							
Specific gravity		1.166	0.951	1.500	0.907	1.149	1.253
Ash-db, %		8.40	0.76	13.65	0.41	0.24	...
Volatiles, %		0.47	0.05	0.81	0.10	0.18	0.24
Extractables-db, %		22.78	0.75	11.23	3.68	1.09	≤0.6
Physical properties:							
Average thickness, mil		58.6	20.3	32.0	28.0	20.1	20.4
Tensile at yield, psi	Machine	...	...	...	1925	960	3330
	Transverse	...	...	...	1865	950	3180
Elongation at yield, %	Machine	...	...	...	20	55	25
	Transverse	...	...	...	20	48	25
Tensile at break, psi	Machine	1780	3655	1990	5885	6080	8500
	Transverse	1705	3500	1800	5330	5750	8410
Tensile at break, ppi	Machine	103.5	74.5	60.9	159.9	122.9	175.1
	Transverse	97.8	71.1	54.8	146.6	115.0	170.0
Elongation at break, %	Machine	425	615	340	405	889	539
	Transverse	465	770	325	430	851	534
Stress at 100% elongation, psi	Machine	445	880	480	1930	920	2770
	Transverse	355	725	450	1785	905	2700
Stress at 100% elongation, ppi	Machine	26.0	18.0	14.7	52.4	18.6	14.3
	Transverse	20.5	14.7	13.6	49.1	18.1	13.7
Stress at 200% elongation, psi	Machine	965	1025	1110	3005	955	2860
	Transverse	815	790	1020	2449	945	2880
Stress at 200% elongation, ppi	Machine	56.2	20.9	33.9	81.6	19.3	14.7
	Transverse	46.8	16.0	31.1	68.5	18.9	14.6
Modulus of elasticity, psi	Machine	...	...	...	36,300	...	...
	Transverse	...	...	...	36,100	...	...
Tear strength-Die C, ppi	Machine	204	336	148	559	500	972
	Transverse	214	363	142	547	523	991
Puncture resistance:							
Thickness, mil		59.5	20.4	33.4	28.9	20.0	21.2
Maximum stress-avg., lb		49.9	50.0	32.0	55.6	41	67
Elongation, in.		1.05	2.08	0.88	0.72	1.85	0.97
Hardness, Durometer points		62A	30A	57A	89A	37A	59A
Hardness, Durometer points		20D	...	...	43D	...	...

[a] EPDM = ethylene propylene rubber; EVA = ethylene vinyl acetate; PB = polybutylene; PEL = polyester elastomer.

[b] Serial number assigned by Matrecon to each lot of sheeting received.

[c] TP = thermoplastic; AM = amorphous; CX = semicrystalline; XL = crosslinked.

TABLE B-8. ANALYTICAL AND PHYSICAL PROPERTIES OF LOW-DENSITY POLYETHYLENE, LINEAR LOW-DENSITY POLYETHYLENE, HIGH-DENSITY POLYETHYLENE, AND HIGH-DENSITY POLYETHYLENE ALLOY SHEETINGS

Polymer[a]		LDPE	LLDPE	HDPE	HDPE	HDPE	HDPE-A
Liner number[b]		309A	284	184	263	305	181
Nominal thickness, mil		20	30	30	80	30	30
Type of compound[c]		CX	CX	CX	CX	CX	CX
	Direction of test						
Analytical Properties:							
Specific gravity		0.938	0.929	0.951	0.953	0.954	0.949
Ash-db, %		...	0.07	0	...	0.69	0.32
Volatiles, %		0.07	0.09	0.13	0.13	0.22	0.11
Extractables-db, %		1.85	0.65	0.73	≤0.60	0.98	2.09
Physical properties:							
Average thickness, mil		22.9	34.4	29.2	82.8	27.9	33.5
Tensile at yield, psi	Machine	...	1505	3885	3030	2540	1975
	Transverse	...	1540	4495	2910	2820	2070
Elongation at yield, %	Machine	...	23	20	20	25	20
	Transverse	...	23	15	20	25	15
Tensile at break, psi	Machine	2660	5360	5215	4260	4110	3915
	Transverse	2765	5420	3830	4275	4390	3945
Tensile at break, ppi	Machine	59.3	185	146	350	114	130
	Transverse	61.4	186	107	359	123	129
Elongation at break, %	Machine	470	765	930	805	760	875
	Transverse	575	800	745	845	770	910
Stress at 100% elongation, psi	Machine	1625	1505	2810	2100	2090	1635
	Transverse	1495	1470	2755	1970	1945	1640
Stress at 100% elongation, ppi	Machine	36.2	52.0	78.6	173	58.2	54.5
	Transverse	33.2	50.5	77.1	165	54.7	53.8
Stress at 200% elongation, psi	Machine	1705	1430	2830	2085	2125	1640
	Transverse	1485	1405	2830	1965	1975	1650
Stress at 200% elongation, ppi	Machine	38.0	49.4	79.2	171	59.1	54.6
	Transverse	33.0	48.1	79.2	165	55.5	54.2
Modulus of elasticity, psi	Machine	25,700	49,000	122,000	98,500	...	59,900
	Transverse	29,100	45,800	150,000	91,700	90,800	65,100
Tear strength-Die C, ppi	Machine	496	613	892	854	764	760
	Transverse	442	601	864	846	725	732
Puncture resistance:							
Thickness, mil		23.9	34.7	30.1	81.9	28.0	33.5
Maximum stress-avg., lb		28.8	60.2	48.0	109.2	43.4	45.5
Elongation at puncture, in.		0.71	1.13	0.65	0.55	0.77	0.56
Hardness, Durometer points		...	91A	94A	...	...	90A
Hardness, Durometer points		42D	47D	60D	57D	52D	51D

[a] LDPE = low-density polyethylene; LLDPE = linear low-density polyethylene; HDPE = high-density polyethylene; HDPE-A = HDPE/ethylene propylene rubber alloy.

[b] Serial number assigned by Matrecon to each lot of sheeting received.

[c] CX = semicrystalline.

TABLE B-9. ANALYTICAL AND PHYSICAL PROPERTIES OF POLYURETHANE, POLYVINYL CHLORIDE, ELASTICIZED POLYVINYL CHLORIDE, AND OIL-RESISTANT POLYVINYL CHLORIDE SHEETINGS

Polymer[a]		Polyurethane	PVC	PVC-E	PVC-OR
Liner number[b]		351	153	176R	144
Nominal thickness, mil		...	30	30	30
Type of compound[c]		TP/AM	TP/AM	TP/AM	TP/AM
Thread count, epi[d]		na	na	20x20	na
	Direction of test				
Analytical Properties:					
Specific gravity		1.118	1.263	1.219	1.356
Ash-db, %		...	5.31	5.12	10.82
Volatiles, %		0.65	0.38	0.44	0.21
Extractables-db, %		1.50	34.57	9.13	30.97
Physical properties:					
Average thickness, mil		15.0	29.4	36.1	32.8
Tensile at fabric break, ppi	Machine	...	...	342	...
	Transverse	...	...	349	...
Elongation at fabric break, %	Machine	...	...	24	...
	Transverse	...	...	22	...
Tensile at break, psi	Machine	7775	2860	...	2655
	Transverse	7040	2540	...	2275
Tensile at break, ppi	Machine	134	94.3	342	86.0
	Transverse	122	83.9	349	74.9
Elongation at break, %	Machine	500	315	24	365
	Transverse	525	335	22	355
Stress at 100% elongation, psi	Machine	1020	1495	...	1235
	Transverse	955	1315	...	1085
Stress at 100% elongation, ppi	Machine	17.6	49.2	...	40.1
	Transverse	16.5	43.5	...	35.7
Stress at 200% elongation, psi	Machine	1305	2120	...	1800
	Transverse	1145	1835	...	1560
Stress at 200% elongation, ppi	Machine	22.5	70.0	...	58.3
	Transverse	19.8	60.6	...	51.3
Tear strength-Die C, ppi	Machine	420	346	...	323
	Transverse	446	343	...	277
Puncture resistance:					
Thickness, mil		15.0	33.3	36.3	33.0
Maximum stress-avg., lb		72.2	44.3	101.5	33.9
Elongation at puncture, in.		2.00	0.69	0.32	0.66
Hardness, Durometer points		86A	73A	93A	72A
Hardness, Durometer points		33D	28D	42D	24D

[a] PVC = polyvinyl chloride: PVC-E = elasticized polyvinyl chloride; PVC-OR = oil-resistant polyvinyl chloride.

[b] Serial number assigned by Matrecon to each lot of sheeting received; R = fabric-reinforced sheeting.

[c] TP = thermoplastic; AM = amorphous.

[d] na = not applicable.

- D792-66(79), "Test Methods for Specific Gravity and Density of Plastics by Displacement."
- D882-83, "Tests Methods for Tensile Properties of Thin Plastic Sheeting."
- D1004-66(81), "Test Methods for Initial Tear Resistance of Plastic Film and Sheeting."
- D2240-86, "Test Method for Rubber Property - Durometer Hardness."

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National Sanitation Foundation. 1985. Standard Number 54: Flexible Membrane Liners. Rev. Standard. National Sanitation Foundation, Ann Arbor, MI.

U.S. General Services Administration. 1980. Method 2065: Puncture Resistance and Elongation Test (1/8-Inch Probe Method). In: Federal Test Method Standard 101C. U.S. General Services Administration, Washington, D.C.

APPENDIX C

EQUILIBRIUM VOLUME SWELLING OF THE POLYMERIC SPECIMENS IMMERSED IN 30 ORGANICS AND IN WATER

Results of determining the equilibrium "volume" swelling of the polymeric specimens immersed in 30 organics and in water are presented in the following tables:

- Table C-1. Equilibrium Volume Swelling of the CPE and CSPE Specimens Immersed in 30 Organics and in Water.
- Table C-2. Equilibrium Volume Swelling of the ECO, EPDM, EVA, CR, NBR, PEL, and PB Specimens Immersed in 30 Organics and in Water.
- Table C-3. Equilibrium Volume Swelling of the LDPE, LLDPE, HDPE, HDPE-A, PU, PVC, PVC-E, and PVC-OR Specimens Immersed in 30 Organics and in Water.

Reported data are the calculated "volume" increases based on the weight gained by the specimen, corrected for the density of the respective organics and water. They do not include any adjustment for the initial density of the specimen, nor do they include any adjustment for loss of plasticizer or any other material that may have been extracted from the original specimens. Adjustment for loss of extracted components would have required extraction tests of specimens after they were dried out.

TABLE C-1. EQUILIBRIUM VOLUME SWELLING OF THE CPE AND CSPE SPECIMENS IMMERSED IN 30 ORGANICS AND IN WATER

Organic	Hildebrand solubility parameter (δ_o)	Liner-polymer/ID number/extractables, %								
		CPE 195 14.85[b]	CPE 335R 4.48	CPE 378R 7.94	CSPE 169R 11.29	CSPE 174R 7.15[c]	CSPE DOY-3[a] <1.0[d]	CSPE DOZ-2[a] <1.0[d]	CSPE DPO[a] <1.0[d]	CSPE DPP[a] <1.0[d]
Isooctane (Ref. Fuel A)	7.0	4.24	10.1	5.83	1.50	8.71	22.8	11.5	17.8	21.1
n-Octane	7.6	6.08	12.5	6.40	1.77	12.9	31.7	14.5	24.3	28.2
Cyclohexane	8.2	26.6	51.0	16.8	119.5	99.7	137.4	D[e]	192.6	273.4
Methyl isobutyl ketone	8.3	D[e]	188.5	D[e]	38.4	40.8	95.5	63.8	93.1	118.6
Isoamyl acetate	8.4	D[e]	200.0	D[e]	42.1	45.4	105.5	89.3	102.9	135.8
o-Xylene	8.8	41.2	D[e]	53.0	577.2	153.2	291.5	D[e]	448.2	751.2
Diethyl carbonate	8.8	87.1	72.5	27.0	8.61	13.2	30.2	20.0	26.7	33.1
Dioctyl phthalate	8.9	361.9	218.1	141.7	32.0	29.2	73.7	52.4	65.1	100.4
Ethyl acetate	8.9	D[e]	137.5	107.4	10.7	16.5	36.5	24.8	32.3	39.6
Methyl ethyl ketone	9.3	D[e]	137.9	282.0	20.4	26.8	58.4	36.3	53.0	67.6
Trichloroethylene	9.3	D[e]	D[e]	62.7	435.0	D[e]	325.6	D[e]	508.9	820.8
Cyclohexanone	9.6	D[e]	251.3	121.4	139.4	101.5	190.1	205.9	240.8	359.0
Acetone	9.8	102.9	56.3	85.0	7.56	13.3	24.5	17.1	21.7	28.2
Tetralin	9.8	D[e]	D[e]	D[e]	353.5	180.9	279.5	D[e]	523.1	765.7
Tetrachloroethylene	9.9	122.6	D[e]	45.2	468.3	160.8	263.1	D[e]	446.1	718.4
2-ethyl-1-hexanol	9.9	4.57	3.96	8.58	1.52	3.12	3.30	1.46	2.35	3.45
Diethyl phthalate	10.0	191.4	125.2	72.7	9.57	14.0	21.4	15.8	18.5	24.2
Quinoline	10.8	D[e]	D[e]	D[e]	96.8	79.8	159.1	202.7	161.6	234.7
Cyclohexanol	10.9	2.13	2.96	7.91	2.40	5.65	9.24	1.78	3.01	4.46
N,N-dimethylacetamide	11.1	D[e]	17.3	62.0	17.8	20.9	51.5	30.1	33.2	38.6
m-Cresol	11.1	67.9	48.5	23.1	14.8	19.6	42.8	30.6	22.9	27.3
Nitroethane	11.1	58.8	38.2	38.5	3.97	7.64	15.3	11.9	11.7	14.4
Benzyl alcohol	11.6	35.2	27.4	9.56	6.87	8.79	37.3	11.4	8.22	9.95
Furfuryl alcohol	11.9	17.6	6.00	1.66	3.82	5.39	20.9	4.37	2.98	3.74
1-Propanol	12.0	2.13	5.42	9.12	2.03	3.13	13.9	2.25	2.01	3.30
Butyrolactone	12.9	93.8	46.9	90.2	4.38	7.31	11.9	8.85	7.66	10.2
Propylene-1,2-carbonate	13.3	23.0	9.08	13.6	1.37	5.63	1.24	1.25	1.94	2.72
2-Pyrrolidone	13.9	111.6	38.8	107.1	12.2	11.2	24.8	8.92	6.38	12.6
Methanol	14.5	3.56	9.27	3.91	7.61	4.58	49.9	8.90	9.54	15.4
Ethylene glycol	16.1	2.21	3.64	5.33	2.06	3.22	2.32	0.57	1.47	3.53
Water	23.4	3.99	6.14	8.91	6.50	4.44	15.4	3.00	6.02	5.33

[a] Laboratory-prepared compounds, the compositions of which are presented in Appendix B.

[b] With n-heptane.

[c] With acetone.

[d] Calculated from compound formulation.

[e] D = dissolved or disintegrated.

TABLE C-2. EQUILIBRIUM VOLUME SWELLING OF THE ECO, EPDM, EVA, CR, NBR, PEL, AND PB SPECIMENS IMMERSED IN 30 ORGANICS AND IN WATER

Organic	Hildebrand solubility parameter (δ_0)	Liner-polymer/ID number/extractables, %							
		ECO 178 7.63	EPDM 232 22.78	EVA 308A 0.75	CR 168 11.23[b]	NBR DPN[a] <1.0[c]	PEL 316 1.09[d]	PEL 323 ≤0.6	PB 221A 3.68
Isooctane (Ref. Fuel A)	7.0	0.53	68.6	28.3	0.96	9.84	7.25	0.86	25.0
n-Octane	7.6	0.98	86.8	34.1	0.61	10.9	8.27	2.88	26.3
Cyclohexane	8.2	6.35	125.9	97.4	30.8	30.7	19.0	4.46	61.6
Methyl isobutyl ketone	8.3	67.4	5.20	3.67	56.1	425.7	38.3	10.5	9.63
Isoamyl acetate	8.4	71.3	5.70	27.6	66.0	246.6	41.3	10.5	12.9
o-Xylene	8.8	64.3	103.1	125.6	109.0	256.9	105.5	17.1	28.9
Diethyl carbonate	8.8	66.6	5.08	15.5	25.9	199.0	40.3	11.0	6.44
Dioctyl phthalate	8.9	25.1	4.16	12.6	73.4	191.6	18.0	0.72	2.50
Ethyl acetate	8.9	87.6	4.96	17.8	33.7	317.1	44.3	11.6	7.30
Methyl ethyl ketone	9.3	88.7	8.33	18.8	39.4	496.8	52.3	12.9	6.53
Trichloroethylene	9.3	102.6	135.4	249.0	123.1	516.4	D[e]	25.1	42.5
Cyclohexanone	9.6	121.4	3.00	28.4	111.9	701.2	123.5	15.8	9.56
Acetone	9.8	75.0	0.88	14.5	10.1	354.0	33.5	11.2	21.7
Tetralin	9.8	154.2	68.6	82.2	180.9	546.8	280.3	24.7	3.26
Tetrachloroethylene	9.9	22.4	146.0	181.8	105.4	90.0	70.9	14.5	17.5
2-ethyl-1-hexanol	9.9	5.01	4.83	15.2	5.27	36.1	16.7	1.51	1.46
Diethyl phthalate	10.0	97.5	0.50	6.28	33.9	475.8	38.0	3.22	0.80
Quinoline	10.8	127.0	4.92	26.2	97.7	672.1	274.0	21.6	5.22
Cyclohexanol	10.9	7.32	7.46	9.19	2.32	35.0	16.7	2.40	2.07
N,N-dimethylacetamide	11.1	127.0	3.93	7.32	60.3	611.5	60.7	16.5	1.97
m-Cresol	11.1	183.8	2.72	55.5	27.2	D[e]	D[e]	D[e]	1.60
Nitroethane	11.1	99.5	0.70	9.33	3.08	439.2	56.1	13.7	2.47
Benzyl alcohol	11.6	123.4	0.38	11.4	13.2	473.7	194.3	17.1	0.85
Furfuryl alcohol	11.9	120.5	0.24	4.54	1.99	251.4	174.6	15.3	0.23
1-Propanol	12.0	4.97	6.40	7.41	3.84	26.9	14.8	7.28	1.15
Butyrolactone	12.9	108.9	0.00	2.69	3.11	362.5	22.5	9.73	0.52
Propylene-1,2-carbonate	13.3	80.3	0.80	1.06	0.11	131.2	8.30	3.30	0.95
2-Pyrrolidone	13.9	100.0	1.29	1.97	14.9	151.8	14.6	4.67	0.61
Methanol	14.5	13.7	1.59	5.89	12.7	19.5	14.7	4.72	0.98
Ethylene glycol	16.1	9.30	0.49	1.55	1.76	9.48	2.42	1.67	0.69
Water	23.4	23.6	1.18	0.66	6.55	9.15	2.62	2.13	1.53

[a] Laboratory-prepared compounds, the compositions of which are presented in Appendix B.

[b] With n-heptane.

[c] With acetone.

[d] Calculated from compound formulation.

[e] D = dissolved or disintegrated.

TABLE C-3. EQUILIBRIUM VOLUME SWELLING OF THE LDPE, LLDPE, HDPE, HDPE-A, PU, PVC, PVC-E, AND PVC-OR SPECIMENS IMMERSED IN 30 ORGANICS AND IN WATER

Organic	Hildebrand solubility parameter (δ_o)	Liner-polymer/ID number/extractables, %										
		LDPE 309A 185[a]	LLDPE 284 0.65[b]	HDPE 184 0.73[b]	HDPE 263 ≤0.6[b]	HDPE 305 0.98[b]	HDPE-A 181 2.09[b]	PU 351 1.50[c]	PVC 153 34.57[d]	PVC DPQ[a] 40.12[d]	PVC-E 176R 9.13[e]	PVC-OR 144 30.97[d]
Isooctane (Ref. Fuel A)	7.0	10.1	11.4	7.06	4.36	7.89	15.9	4.76	21.7	22.1	3.25	1.83
n-Octane	7.6	13.1	14.2	8.49	7.68	9.68	18.6	6.79	19.9	20.3	2.70	1.79
Cyclohexane	8.2	23.1	24.5	11.8	11.2	12.8	34.7	19.8	19.9	16.4	14.2	4.94
Methyl isobutyl ketone	8.3	3.67	4.49	3.62	2.27	4.23	4.36	95.8	D[f]	D[f]	D[f]	D[f]
Isoamyl acetate	8.4	6.52	6.18	4.24	2.75	6.34	7.72	63.4	245.4	D[f]	D[f]	230.6
o-Xylene	8.8	19.9	20.4	12.6	11.6	14.3	28.8	71.7	7.92	17.3	84.0	11.1
Diethyl carbonate	8.8	4.56	2.61	2.37	2.15	2.69	2.96	56.5	11.8	23.8	42.6	10.2
Dioctyl phthalate	8.9	2.71	0.92	0.46	0.64	0.49	3.12	24.3	176.4	143.7	55.6	193.7
Ethyl acetate	8.9	3.01	3.04	2.63	2.61	2.61	3.27	85.1	147.5	D[f]	D[f]	150.8
Methyl ethyl ketone	9.3	2.72	4.06	2.53	2.17	2.55	3.42	214.9	D[f]	D[f]	D[f]	D[f]
Trichloroethylene	9.3	19.9	21.5	10.5	10.9	11.8	32.1	129.3	17.0	27.6	109.4	22.5
Cyclohexanone	9.6	5.04	4.36	3.03	1.40	4.88	5.40	D[f]	D[f]	D[f]	D[f]	D[f]
Acetone	9.8	3.23	1.98	2.42	1.23	1.64	1.41	92.9	171.9	D[f]	D[f]	177.0
Tetralin	9.8	11.5	12.3	7.67	6.80	1.88	16.9	233.3	111.0	D[f]	D[f]	124.4
Tetrachloroethylene	9.9	25.0	25.5	13.7	13.7	13.5	41.4	53.4	2.64	0.19	64.1	16.5
2-ethyl-1-hexanol	9.9	4.21	1.59	0.52	0.32	1.06	1.44	42.3	12.8	3.02	8.34	6.08
Diethyl phthalate	10.0	0.81	1.36	0.89	0.45	1.37	1.35	80.3	86.58	124.3	56.3	93.9
Quinoline	10.8	3.67	4.06	3.30	1.79	4.22	5.33	D[f]	D[f]	D[f]	D[f]	D[f]
Cyclohexanol	10.9	2.07	1.71	0.86	0.40	1.21	1.81	51.8	11.2	0.37	9.61	2.11
N,N-dimethylacetamide	11.1	2.44	3.93	1.67	0.52	2.47	2.02	D[f]	D[f]	D[f]	D[f]	D[f]
m-Cresol	11.1	2.17	1.59	2.72	0.79	2.39	1.18	D[f]	7.65	0.68	93.1	7.32
Nitroethane	11.1	1.12	0.94	1.17	0.60	0.90	1.89	50.4	44.3	81.8	D[f]	40.3
Benzyl alcohol	11.6	0.76	0.44	0.94	0.17	0.91	0.61	D[f]	11.8	9.53	52.2	1.68
Furfuryl alcohol	11.9	0.20	0.16	0.22	0.70	0.39	0.06	735.8	13.1	11.3	23.1	6.22
1-Propanol	12.0	1.01	1.05	0.77	0.68	1.15	1.34	41.0	19.0	19.4	5.04	5.44
Butyrolactone	12.9	0.26	0.66	0.37	0.16	0.71	0.19	180.4	D[f]	D[f]	53.4	178.6
Propylene-1,2-carbonate	13.3	0.52	0.75	0.28	0.24	0.24	0.9	13.0	11.9	27.8	16.1	15.5
2-Pyrrolidone	13.9	0.79	0.79	0.86	0.16	0.90	0.54	D[f]	277.7	D[f]	42.9	258.0
Methanol	14.5	3.46	1.74	1.40	1.09	2.60	2.86	34.4	17.7	11.7	2.98	17.6
Ethylene glycol	16.1	0.56	0.41	0.41	0.24	0.39	0.43	6.95	3.43	4.89	3.12	4.32
Water	23.4	4.61	1.54	0.62	0.23	1.51	1.60	1.66	1.58	4.17	2.32	2.65

[a] Laboratory-prepared compounds, the compositions of which are presented in Appendix B.

[b] With methyl ethyl ketone.

[c] With n-heptane.

[d] With 2:1 mixture of CCl_4 and CH_3OH.

[e] With CH_3OH.

[f] D = dissolved or disintegrated.

APPENDIX D

EQUIPMENT, MATERIALS, AND CONDITIONS USED IN GAS CHROMATOGRAPHIC ANALYSIS

A Perkin-Elmer Sigma Three Series gas chromatograph with a flame ionization detector was used for all the gas chromatographic analyses. The instrument was fitted with different columns as required to effect separation of the different mixtures of volatile and semivolatile organics. Different temperature programs for both the oven and the injection/detection ports were also used to maximize separation and response factors for the mixtures. The different conditions, injection volumes, carrier gas flow rates, etc., are all presented in Table D-1.

The concentrations of the organics in the leachates, extractables, and the vapors from the FMLs were determined by comparing peak height values with calibration curves. The calibration curves for the leachates were determined by injecting 1 µL of various solutions of known concentrations of the different organics into the gas chromatograph (GC) column. Injections of each standard were performed five times to ensure reproducibility of injection techniques. Standard deviation was 2%. A typical calibration curve for GC peak heights vs. concentration of organics in solutions of known concentrations is presented in Figure D-1. The calibration curves for the headspace (HSGC) analyses were prepared by analyzing a specific volume of vapor (either 100 µL or 400 µL from headspace cans injected with different volumes of a standard solution of organics. A typical calibration curve for GC peak heights vs. concentrations of organics in a vapor is presented in Figure D-2.

Hamilton syringes were used for all sampling and analyses. The Model No. 701N 10-µL syringe was used for all aqueous and extractables sampling and the Models No. 1001 100-µL and No. 710 1-mL syringes were used for sampling of headspace containers and vapor compartments in the partitioning apparatus.

The gases used in the analyses were obtained from either Matheson, Inc. or Wel-Med, Inc. Prepurified helium was always used as a carrier gas equipped with an oxygen trap to remove any traces of oxygen in the carrier gas. USP grade oxygen was used to burn the reagent-grade hydrogen in the flame ionization detector.

TABLE D-1. CONDITIONS USED IN GAS CHROMATOGRAPHIC ANALYSES

Set of conditions	Experiment	Types of samples	Column	Oven temperature program, °C/time	Injection port and detector temperature, °C	Injection volume, µL	Carrier gas (He) flow rate, mL/min.	O_2/H_2, psi
1	Preliminary experiments and compatibility tests	Leachate, extractables, vapor	6 ft x 1/8 in. SS; 100% OV-101 on 100/120 mesh Supelcoport	30° to 120°C at 10°C/min.	250	Liquid: 1; Vapor: 400	30	40/30
2	Polyethylene specimens saturated with organics and placed in water	Leachate, vapor	6 ft x 1/8 in. SS; 10% Carbowax 20M on 80/100 mesh Supelcoport	60°C for 1 min. to 140°C at 20°C/min.	250	Liquid: 1; Vapor: 400	30	40/30
3	Two-compartment apparatus with water spiked with nine organics	Leachate, vapor	12 ft x 1/8 in. SS; 10% Carbowax 20M on 80/100 mesh Gas-Chrom R	60°C to 140°C at 20°C/min.	250	Liquid: 1; Vapor: 100	30	40/30
4	Two-compartment apparatus with water spiked with TCE	Leachate, vapor	12 ft x 1/8 in. SS; 10% Carbowax 20M on 80/100 mesh Gas-Chrom R	Isothermal at 120°C	250	Liquid: 1; Vapor: 100	8	40/30
5	Three-compartment apparatus with water spiked with TCE and toluene	Leachate, vapor	DB WAX-1, 15M, polyethylene glycol, fused silica open tube (FSOT)	60° to 160°C at 20°C/min.	275	Liquid: 1; Vapor: 100	8	40/30
6	Three-compartment apparatus with water spiked with six organics	Leachate, vapor	DB WAX-1, 15M, polyethylene glycol, fused silica open tube (FSOT)	60° to 160°C at 20°C/min.; 2 min. at 160°C	275	Liquid: 1; Vapor: 100	8	40/30

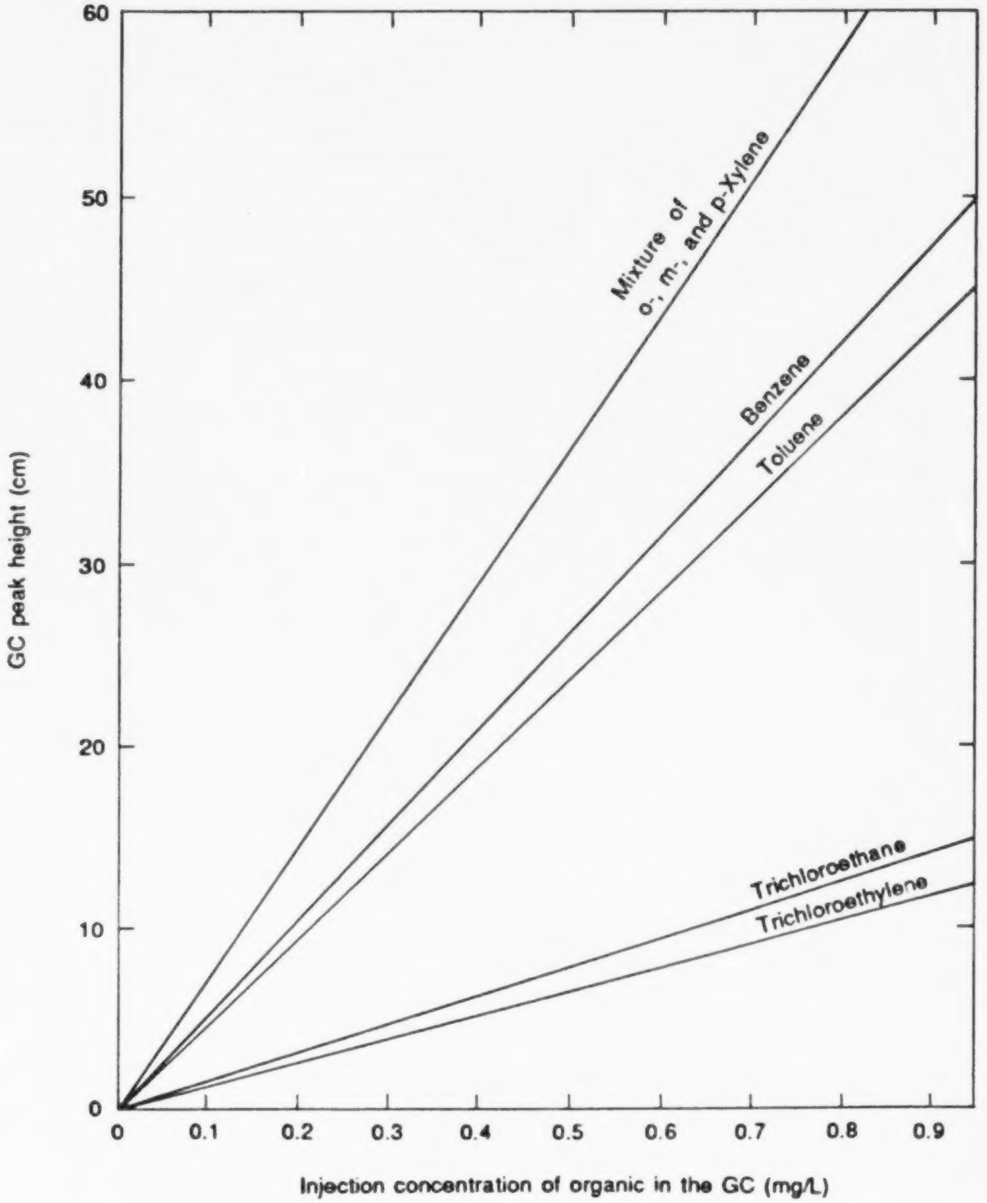

Figure D-1. Typical calibration curves for GC peak heights vs. concentrations of organics in aqueous solution standards containing equal weights of TCA, benzene, TCE, toluene, and a mixture of xylenes in an aqueous solution.

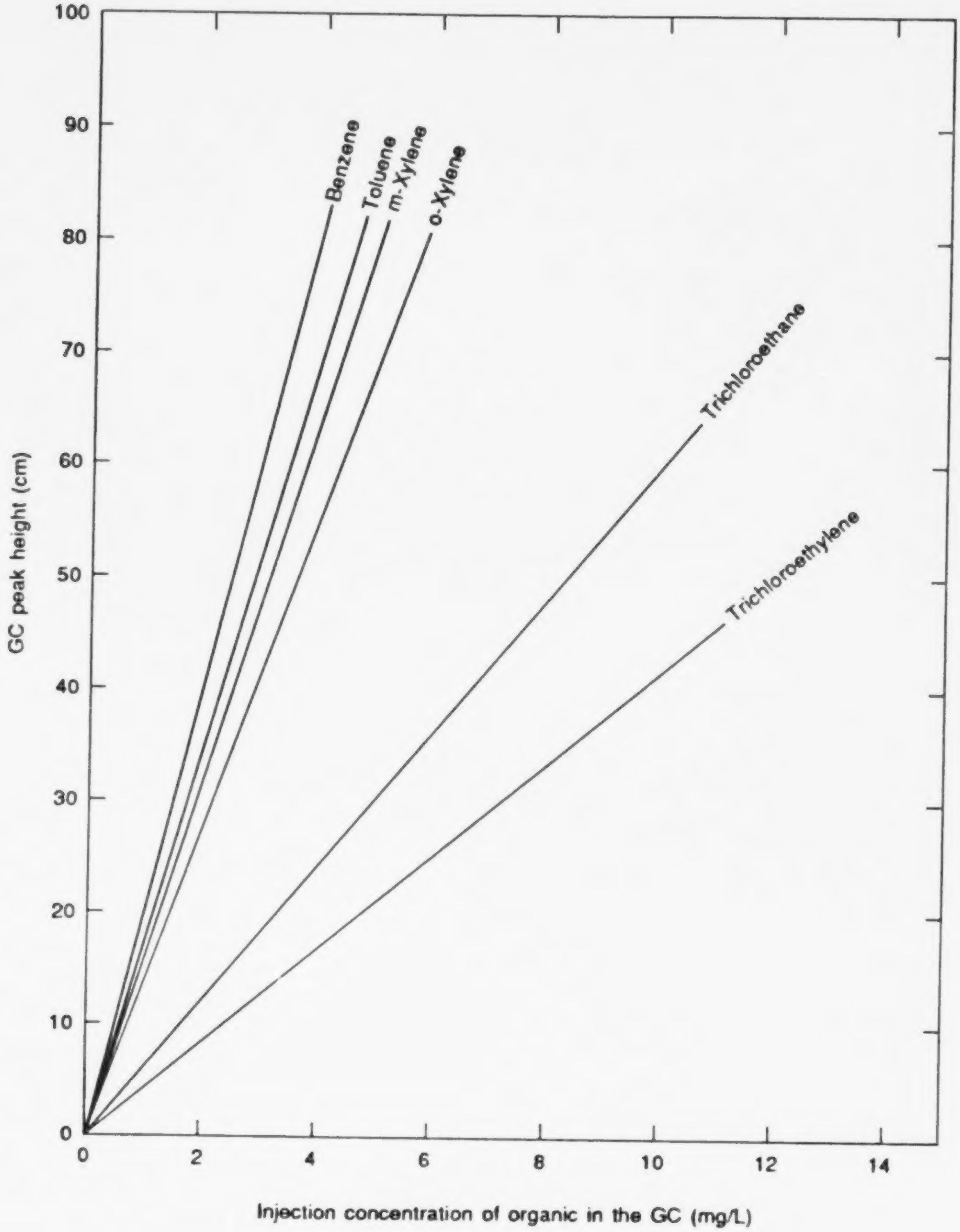

Figure D-2. Typical calibration curves for GC peak heights of various organics as a function of the concentration of the organic vapor in a headspace can.

APPENDIX E

ORGANICS USED IN PARTITIONING/PERMEABILITY EXPERIMENTS WITH DILUTE AQUEOUS SOLUTIONS

Organic	Source	Purity, %	Mole-cular weight	Density at 20°C, g/cm^3	Specific volume, cm^3/g	Boiling point, °C	Vapor pressure at 25°C, mm Hg	Solubility parameters[a] δ_o	δ_d	δ_p	δ_h	Solu-bility in water, mg/L[b]	CASNO[c]	In EPA list[d]
Aliphatic hydrocarbon														
n-Octane	Gold Label Aldrich	99+	114.23	0.703	1.422	125.7	16.71	7.6	7.6	0.0	0.0	6.6	111-65-9	No
Aromatic hydrocarbons														
Benzene	EM Science	99.9	78.11	0.879	1.138	80.1	96.43	9.2	9.0	0.0	1.0	1,178	71-43-2	Yes
Toluene	Mallinkrodt	99.9	92.13	0.866	1.155	110.6	31.96	8.9	8.8	0.7	1.0	515	108-86-3	Yes
o-Xylene	J. T. Baker	99.0	106.16	0.897	1.115	144.0	8.22	8.8	8.7	0.5	1.5	175	1330-20-7	Yes
m-Xylene	MCB[e]	98.0	106.16	0.868	1.152	139.3	9.15	8.6	8.4	0.5	1.2	196	1330-20-7	Yes
p-Xylene	Spectrum	98+	106.16	0.854	1.171	137-138	9.41	8.6	8.4	0.5	0.1	190	1330-20-7	Yes
Chlorinated hydrocarbons														
1,1,1-Trichlorethane	MCB[e]	99.9	133.42	1.338	0.748	74.1	143.35	8.6	8.3	2.1	1.0	1,320	71-55-6	Yes
Trichloroethylene	Mallinkrodt	99.9	131.40	1.476	0.677	87.2	80.30	9.2	8.8	1.5	2.6	1,100	79-01-6	Yes
Oxygenated hydrocarbons														
Propionic acid	Mallinkrodt	...	74.08	0.993	1.007	141.1	6.23	12.4	7.5	5.5	8.4	∞	...	No
Acetone	Mallinkrodt	99.98	58.08	0.788	1.269	56.5	263.2	9.9	7.6	5.1	3.4	∞	67-64-1	Yes
Methyl ethyl ketone	Mallinkrodt	99.98	72.10	0.805	1.242	79.6	100.0	9.3	7.8	4.4	2.5	240,000	78-93-6	Yes
n-Butyl alcohol	Kodak	99.4	74.12	0.810	1.235	117.7	8.50	11.3	7.8	2.8	7.7	74,500	71-36-6	Yes
n-Butyric acid[f]	...	...	88.11	0.964	1.037	162.0	1.00	10.5	7.3	2.0	5.2	∞	107-92-6	Yes
Esters														
Tri-n-butyl phosphate	FMC Corporation	...	266.32	0.976	1.025	289.0	$\sim 10^{-6}$	8.8	8.0	3.1	2.1	6,060	126-73-8	No
Di(ethylhexyl) phthalate	Harwick	...	390.57	0.984	1.016	231.0	3.4×10^{-7}	8.9	8.1	3.4	1.5	0.4	117-81-7	No

[a] Barton (1983).

[b] Riddick and Bunger (1970).

[c] Chemical Abstract Services' number.

[d] EPA list of volatile contaminants (Appendix F).

[e] Matheson, Coleman, and Bell.

[f] n-Butyric acid was the oxidation product of n-butanol observed in the partitioning experiment described in Section 6.

APPENDIX F

ORGANICS IDENTIFIED BY THE EPA AS VOLATILE CONTAMINANTS[a]

Compound	CASNO[b]
Acetone	67-64-1
Acrylonitrile	107-13-1
Benzene	71-43-2
n-Butyl alcohol	71-36-6
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[a] Includes compounds identified in both the Land Disposal Restrictions Rule and the Toxicity Characteristic.

[b] Chemical Abstracts Services number.

Source: EPA (1986).

APPENDIX G

EPA METHOD 9090 TESTING OF HDPE FMLS

EPA Method 9090 assesses the compatibility of FMLs and waste liquids. In this test, FML samples in slab form are immersed for up to four months at room temperature (23°C) and at 50°C in a representative sample of a waste liquid or leachate. Testing is performed on the unexposed membrane for baseline data and on samples exposed to the waste liquid for 30, 60, 90, and 120 days to assess the effects of the immersion. On completion of the testing, the data are reviewed and analyzed to determine whether any changes in the properties of the FML may critically affect its performance in the proposed use or whether results indicate projections of inadequate performance.

The 1984 version of EPA Method 9090 (EPA, 1984), noticed in the Federal Register of October 1, 1984, was in effect at the time the work on this project was performed. A revised version of the EPA Method 9090 was published in 1986 in SW-846 (EPA, 1986). Many of the additional tests in the testing described in Section 7 of this report and which were not in the 1984 version of the method were incorporated in the 1986 version. This appendix describes the testing required in the compatibility testing of an HDPE FML by the 1984 version of Method 9090. It also describes the revisions included in the 1986 version of the method that pertain to the testing of HDPE FMLs.

TESTING OF HDPE SAMPLES

In the compatibility testing of an HDPE FML, the 1984 version of Method 9090 requires that the following testing be performed on both the exposed and unexposed FML:

Property	Test method	Baseline testing	Testing of exposed slabs
		No. of specimens[a]	
Tensile	ASTM D638 (modified)	5M, 5T	3M, 3T
Tear resistance	ASTM D1004	5M, 5T	3M, 3T
Puncture resistance	FTMS 101C, Method 2065	5	2
		No. of readings	
Hardness	ASTM D2240	5[b]	5[b]

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[a] M = machine direction; T = transverse direction.

[b] Number of readings required by the test method.

It also requires measurement of the weight and dimensions of the individual test slabs before and after exposure.

ASTM D638, used to measure tensile properties, is modified to allow for the use of a smaller nonstandard-sized tensile dumbbell having the same cross-sectional area as the Type IV dumbbell of D638. In comparison to the Type IV dumbbell, the "special" dumbbell features reduced tab-end size and shorter length of the narrow test area. When an HDPE FML is being tested, tensile and tear testing are performed with a jaw separation rate of 2 inches per minute (ipm).

In the 1986 version of EPA Method 9090, there are changes in the baseline testing requirements of the testing included in the 1984 version of the method. Furthermore, additional testing of FMLs is required including a test required for semicrystalline materials only, and some additional testing is recommended. The changes in the baseline testing requirements of the tests included in the 1984 version make the number of specimens required for the baseline testing the same as the number of specimens required for the testing of the exposed slabs. Thus, the required number of test specimens is as follows:

Property	Number of specimens required in baseline testing
Tensile	3M, 3T
Tear resistance	3M, 3T
Puncture resistance	2
Hardness	3

---

[a]M = machine direction; T = transverse direction.

The tests that are appropriate to testing HDPE FMLs not in the 1984 version but which are in the 1986 version are as follows:

- Volatiles content, before exposure and after each exposure period, in accordance with Matrecon Test Method 1 (Matrecon, 1983, pp 338-39).
- Extractables, before exposure and after each exposure period, in accordance with Matrecon Test Method 2 (Matrecon, 1983, pp 340-43).
- Modulus of elasticity, before exposure and after each exposure period, two specimens each direction, in accordance with ASTM D882-83 (modified). (Note: Modulus of elasticity testing was required of semicrystalline materials only.)
- Hydrostatic resistance, before exposure and after each exposure period, in accordance with ASTM D751, Method A, Procedure 1. (Note: The number of specimens was not specified, and no provision was made for any hydrostatic resistance test specimens in the suggested cutting pattern for crystalline materials.)

- Specific gravity, before exposure only, three specimens in accordance with ASTM D792, Method A.

The 1986 version of the method also recommends that the potential for environmental stress cracking of semicrystallline FMLs should be determined. Testing should be performed in accordance with either ASTM D1693 or the National Bureau of Standards Constant Tensile Load.

ASTM D882-83, used to measure modulus of elasticity, is modified to allow for the use of a strip specimen measuring 0.5 x 6 in. which is tested with an initial jaw separation of 2.0 inches. ASTM D882-83 defines the test specimen for determining modulus of elasticity as a strip with a nominal width of 0.2 to 1.0 in. and a specimen gage length (i.e. an initial jaw separation) of 10 inches. The method also specifies that the specimens should be tested with an initial strain rate of 0.1 in./in. minute. The modification of the modulus of elasticity procedure in Method 9090 specifies the same initial strain rate. Testing with the longer specimen results in somewhat higher test values. The smaller strip specimen is used in the compatibility test because of the constraints of the exposure sample size.

IMMERSION TANKS

The 1984 version of EPA Method 9090 specified the following for the exposure tanks:

> 4.1 Exposure tanks of a size sufficient to contain the samples with provisions for supporting the specimens so that they do not touch bottom or sides of the tank, or each other, and for stirring the liquid in the tank. The tank shall be equipped with a means of maintaining the solution at temperatures of room temperature and 50°±2°C and for preventing evaporation of the solution (e.g., cover equipped with a reflux condenser) with both sides of the liner material exposed to the chemical environment. If the liner has a side which is not exposed to the waste in actual use and which is not designed to withstand exposure to the chemical environment, then such a liner may be treated with only the barrier surface exposed.

The 1986 version of the method specified the following:

> 4.1 Exposure tank: Of a size sufficient to contain the samples, with provisions for supporting the samples so that they do not touch the bottom or sides of the tank or each other, and for stirring the liquid in the tank. The tank should be compatible with the waste fluid and impermeable to any of the constituents they are intended to contain. The tank shall be equipped with a means for maintaining the solution at room temperature (23°±2°C) and 50°±2°C and for preventing evaporation of the solution (e.g. use a cover equipped with a reflux condenser, or seal the tank with a Teflon gasket and use an airtight cover)...

The revised method, thus, defines room temperature as 23°±2°C. However, other than stating that the tanks should be "compatible with the waste fluid and impermeable to any of the constituents," neither version of the method specifies the material of construction.

MONITORING AND ANALYSIS OF WASTE LIQUID

No requirements were made in either version of Method 9090 for monitoring the concentration levels of the waste liquid in the course of the exposure test and for analyzing the waste liquid to determine the level of safety precautions that need to be taken in handling the waste and to aid in the final interpretation of the results of testing the exposed FML.

REFERENCES

EPA. 1984. Method 9090: Compatibility Test for Wastes and Membrane Liners. Noticed in: Federal Register, Vol. 49, No. 191. NTIS No. PB 85 103-026.

EPA. 1986. Method 9090: Compatibility Test for Wastes and Membrane Liners. In: Test Methods for Evaluating Solid Waste. Vol. 1A: Laboratory Manual, Physical/Chemical Methods, 3rd ed. SW-846. U.S. Environmental Protection Agency, Washington, DC.

Matrecon, Inc. 1983. Lining of Waste Impoundment and Disposal Facilities. SW-870 Revised. U.S. EPA, Washington, D.C. 448 pp. GPO #055-00000231-2.

APPENDIX H

ORGANIC CONCENTRATIONS IN THE EXPOSURE TANKS USED IN THE COMPATIBILITY TEST WITH SPIKED WATER

Exposure temperature tank number, and time	Concentration of volatiles in water, mg/L								Concentration of non-volatiles, mg/L	
	Acetone	MEK	1,1,1-TCA	Benzene	TCE	Toluene	m- and p-Xylenes	o-Xylene	TBP	DEHP
Initial spike[a]										
0 day	197	201	326	231	406	338	191	103	251	250
Tank I (23°C)										
33 days (before opening[b,c])	...	301	27	31	33	29	2.5	1.8	30	<1
41 days (after 2nd spike[c,d])	...	201	0	18	32	31	14	8.9	...	...
50 days (after 2nd spike[c,d])	...	311	59	27	60	64	8.9	3.4	51	...
105 days (before opening[b,c])	388	301	0	0	8.85	10.3	16.8	16.5	8.62	<1
139 days (before opening[b,e])	365	307	0	0	0	0	0	0	12.1	<1
Tank III (23°C)										
33 days (before opening[b,c])	...	319	0	23	28	25	10	9.2	13	<1
41 days (after 2nd spike[c,d])	...	505	21	16	34	45	28	9.2	...	...
50 days (after 2nd spike[c,d])	...	340	0	10	21	26	22	10	29	<1
105 days (before openingb[b,c])	350	262	0	0	0	4	5.77	3.27	9.52	<1
139 days (before opening[b,e])	250	210	0	0	0	0	0	0	9.35	<1
Tank II (50°C)										
33 days (before opening[b,c])	...	157	0	8.0	8.4	9.3	7.6	6.7	11	<1
41 days (after 2nd spike[c,d])	...	201	0	2.6	4.2	8.9	11	5.9	...	...
50 days (after 2nd spike[c,d])	...	164	0	0	0	6	16	7	26	<1
105 days (before opening[b,c])	117	70.4	0	0	5.0	0	2.09	1.74	7.1	<1
139 days (before opening[b,e])	80	63	0	0	0	0.1	0	0	6.6	<1
Tank IV (50°C)										
33 days (before opening[b,c])	...	289	0	9.8	9.5	11	6.4	6.3	11.1	<1
41 days (after 2nd spike[c,d])	...	362	0	2.7	5.5	9.6	11	6.1	...	...
50 days (after 2nd spike[c,d])	...	267	0	0	0	3.5	10	5.8	18	<1
105 days (before opening[b,c])	165	103	0	0	4.76	0	1.72	1.02	9.99	<1
139 days (before opening[b,e])	127	86.8	0	0	0	0	0	0	7.15	<1

[a] Total concentration in (mg/L) of the organics injected in the water in two portions. Value assumes complete dissolution in the water.

[b] Samples taken before opening the tanks to recover test slabs.

[c] All leachate was injected into a column with low water resistance, thus the column was degraded with time. Organics that normally were separable on a new column as either vapor from a headspace can or as solutions in a volatile organic solvent, such as methylene chloride, could not be separated or resolved.

[d] Samples taken after addition of second portion of organics.

[e] Methyl ethyl ketone (MEK) and acetone concentrations were high at the end of the experiments. Leachate was analyzed by GC with a fused silica open-tube (FSOT) column which is described in Appendix D. Also, a large amount of tributyl phosphate (TBP) was detected. Virtually no trichloroethane (TCA), trichloroethylene (TCE), toluene, o-, m-, p-xylenes, benzene, or di(ethylhexyl) phthalate (DEHP) were detected in the water after 139 days of exposure to polyethylene.

APPENDIX I

COMPATIBILITY TESTING OF HDPE FML IN SPIKED DEIONIZED WATER

This appendix presents the results of performing compatibility testing of an HDPE with an aqueous solution containing organics. The solution was mixed by spiking deionized water with the following: 1,1,1-trichloroethane, trichloroethylene, benzene, toluene, ortho-, meta- and para-xylenes, acetone, methyl ethyl ketone, di(ethylhexyl) phthalate, and tri-butyl phosphate.

The properties of the HDPE were determined before and after one, two, three, and four months of exposure. Samples were exposed at 23° and 50°C. The results of the testing are presented in the following tables:

- Table I-1. 60-Mil HDPE FML--Unexposed and After One, Two, Three, and Four Months of Exposure at 23°C in Tank I.
- Table I-2. 60-Mil HDPE FML--Unexposed and After One, Two, Three, and Four Months of Exposure at 23°C in Tank III.
- Table I-3. 60-Mil HDPE FML--Unexposed and After One, Two, Three, and Four Months of Exposure at 50°C in Tank II.
- Table I-4. 60-Mil HDPE FML--Unexposed and After One, Two, Three, and Four Months of Exposure at 50°C in Tank IV.

TABLE I-1. COMPATIBILITY TESTING OF HDPE FML IN SPIKED DEIONIZED WATER[a]

60-Mil HDPE FML[b]--Unexposed and After One, Two, Three, and Four Months of Exposure at 23°C in Tank I

Property	Direction of test	Initial values	Exposure time, months			
			1	2	3	4
Analytical properties			Test values			
Volatiles, %		0.09	1.31	1.19	0.99	0.70
Extractables, %		0.65	0.74	0.80	0.83	1.13
Dimensional properties			Percent change			
Weight			+1.2	+1.3	+1.9	+1.6
Thickness			-0.2	+0.2	+0.8	+1.2
Area			+1.2	+0.8	+0.6	+0.5
Physical properties			Percent retention			
Tensile at yield	Machine	2570 psi	104	100	109	103
	Transverse	2700 psi	101	97	107	102
Elongation at yield	Machine	19%	84	79	79	89
	Transverse	19%	79	79	74	79
Tensile at break	Machine	4080 psi	96	99	99	112
	Transverse	4040 psi	105	117	103	101
Elongation at break	Machine	810%	97	100	100	106
	Transverse	780%	104	113	101	104
Stress at 100% elongation	Machine	1790 psi	102	99	105	102
	Transverse	1840 psi	98	95	103	96
Stress at 200% elongation	Machine	1830 psi	101	99	102	100
	Transverse	1920 psi	96	95	101	94
Modulus of elasticity[c]	Machine	111,000 psi	98	102	113	103
	Transverse	118,500 psi	94	94	96	105
Tear strength	Machine	795 ppi	101	99	101	99
	Transverse	785 ppi	100	99	100	100
Puncture resistance[d]			Test values			
Thickness, mil		60.8	63.0	62.5	60.3	62.5
Maximum stress, lb		91.7	89.5	91.8	86.0	95.4
Elongation at puncture, in.		0.59	0.54	0.64	0.54	0.62
			Percent retention			
Stress normalized for 100-mil sheet		151 lb	94	97	95	101
Hydrostatic burst resistance			Test values			
Thickness, mil		64.7	61.3	62.0	61.0	59.9
Maximum stress, lb		557	533	518	507	535
			Percent retention			
Stress normalized for 100-mil sheet		861 psi	101	97	97	104
Hardness, Duro D points			Change in points			
5-second reading		60	-2	-2	-2	-1

[a] The immersion liquid was deionized water spiked with the following: 1,1,1-trichloroethane, trichloroethylene, benzene, toluene, ortho-, meta- and para-xylenes, acetone, methyl ethyl ketone, di(ethylhexyl) phthalate, and tri-butyl phosphate.

[b] Matrecon identification number 392.

[c] Measured using 0.5 x 8-in. strip specimens with an initial jaw separation of 4.0 in. and an initial strain rate of 0.1 in./in. min. Using a specimen with a 10-in. gage length as specified in ASTM D882-83 would result in higher values.

TABLE I-2. COMPATIBILITY TESTING OF HDPE FML IN SPIKED DEIONIZED WATER[a]

60-Mil HDPE FML[b]--Unexposed and After One, Two, Three, and Four Months of Exposure at 23°C in Tank III

Property	Direction of test	Initial values	Exposure time, months			
			1	2	3	4
Analytical properties			Test values			
Volatiles, %		0.09	0.97	0.85	0.58	0.33
Extractables, %		0.65	0.84	1.11	0.82	1.47
Dimensional properties			Percent change			
Weight			+0.8	+1.0	+1.5	+0.5
Thickness			+1.6	+0.6	+0.5	+0.8
Area			+0.8	+0.7	+0.2	+0.2
Physical properties			Percent retention			
Tensile at yield	Machine	2570 psi	104	104	107	108
	Transverse	2700 psi	101	100	104	104
Elongation at yield	Machine	19%	79	79	74	79
	Transverse	19%	79	79	63	74
Tensile at break	Machine	4080 psi	112	100	111	118
	Transverse	4040 psi	87	113	112	102
Elongation at break	Machine	810%	107	102	105	109
	Transverse	780%	96	112	107	104
Stress at 100% elongation	Machine	1790 psi	102	103	105	104
	Transverse	1840 psi	96	96	98	98
Stress at 200% elongation	Machine	1830 psi	102	102	105	103
	Transverse	1920 psi	93	94	96	94
Modulus of elasticity[c]	Machine	111,000 psi	103	104	116	121
	Transverse	118,500 psi	104	95	100	112
Tear strength	Machine	795 ppi	99	101	99	102
	Transverse	785 ppi	99	100	99	100
Puncture resistance[d]			Test values			
Thickness, mil		60.8	63.5	64.5	63.0	63.0
Maximum stress, lb		91.7	93.2	95.7	91.0	94.9
Elongation at puncture, in.		0.59	0.59	0.61	0.56	0.60
			Percent retention			
Stress normalized for 100-mil sheet		151 lb	97	98	95	100
Hydrostatic burst resistance			Test values			
Thickness, mil		64.7	62.7	63.5	63.5	63.3
Maximum stress, lb		557	543	532	534	645
			Percent retention			
Stress normalized for 100-mil sheet		861 psi	101	97	98	118
Hardness, Duro D points			Change in points			
5-second reading		60	-2	-2	-2	-2

[a] The immersion liquid was deionized water spiked with the following: 1,1,1-trichloroethane, trichloroethylene, benzene, toluene, ortho-, meta- and para-xylenes, acetone, methyl ethyl ketone, di(ethylhexyl) phthalate, and tri-butyl phosphate.

[b] Matrecon identification number 392.

[c] Measured using 0.5 x 8-in. strip specimens with an initial jaw separation of 4.0 in. and an initial strain rate of 0.1 in./in. min. Using a specimen with a 10-in. gage length as specified in ASTM D882-83 would result in higher values.

TABLE I-3. COMPATIBILITY TESTING OF HDPE FML IN SPIKED DEIONIZED WATER[a]

60-Mil HDPE FML[b]--Unexposed and After One, Two, Three, and Four Months of Exposure at 50°C in Tank II

Property	Direction of test	Initial values	Exposure time, months			
			1	2	3	4
Analytical properties			Test values			
Volatiles, %		0.09	0.67	0.48	0.37	0.24
Extractables, %		0.65	1.42	1.28	0.65	1.42
Dimensional properties			Percent change			
Weight			+1.3	+0.9	+1.8	+1.5
Thickness			+0.3	+0.5	+0.8	+1.5
Area			+0.6	+0.4	+0.2	+0.5
Physical properties			Percent retention			
Tensile at yield	Machine	2570 psi	105	108	108	112
	Transverse	2700 psi	106	107	108	104
Elongation at yield	Machine	19%	100	79	84	79
	Transverse	19%	79	79	84	79
Tensile at break	Machine	4080 psi	117	107	101	98
	Transverse	4040 psi	105	117	104	117
Elongation at break	Machine	810%	110	103	99	98
	Transverse	780%	104	109	90	112
Stress at 100% elongation	Machine	1790 psi	104	107	106	106
	Transverse	1840 psi	102	103	103	99
Stress at 200% elongation	Machine	1830 psi	105	107	107	107
	Transverse	1920 psi	99	99	101	97
Modulus of elasticity[c]	Machine	111,000 psi	92	91	104	108
	Transverse	118,500 psi	89	93	105	109
Tear strength	Machine	795 ppi	103	104	104	104
	Transverse	785 ppi	101	103	103	102
Puncture resistance[d]			Test values			
Thickness, mil		60.8	64.3	63.3	64.0	63.8
Maximum stress, lb		91.7	97.6	98.9	97.5	99.1
Elongation at puncture, in.		0.59	0.57	0.62	0.57	0.61
			Percent retention			
Stress normalized for 100-mil sheet		151 lb	101	103	101	103
Hydrostatic burst resistance			Test values			
Thickness, mil		64.7	63.3	62.3	64.0	63.1
Maximum stress, lb		557	553	545	610	565
			Percent retention			
Stress normalized for 100-mil sheet		861 psi	102	102	111	104
Hardness, Duro D points			Change in points			
5-second reading		60	-2	-1	-2	-1

[a] The immersion liquid was deionized water spiked with the following: 1,1,1-trichloroethane, trichloroethylene, benzene, toluene, ortho-, meta- and para-xylenes, acetone, methyl ethyl ketone, di(ethylhexyl) phthalate, and tri-butyl phosphate.

[b] Matrecon identification number 392.

[c] Measured using 0.5 x 8-in. strip specimens with an initial jaw separation of 4.0 in. and an initial strain rate of 0.1 in./in. min. Using a specimen with a 10-in. gage length as specified in ASTM D882-83 would result in higher values.

TABLE I-4. COMPATIBILITY TESTING OF HDPE FML IN SPIKED DEIONIZED WATER[a]

60-Mil HDPE FML[b]--Unexposed and After One, Two, Three, and Four Months of Exposure at 50°C in Tank IV

Property	Direction of test	Initial values	Exposure time, months			
			1	2	3	4
Analytical properties			Test values			
Volatiles, %		0.09	0.80	0.37	0.22	0.22
Extractables, %		0.65	0.55	0.87	0.84	1.57
Dimensional properties			Percent change			
Weight			+1.1	+0.7	+0.9	+0.9
Thickness			+1.1	+0.5	+1.1	+1.4
Area			+0.6	+0.4	+0.2	+0.2
Physical properties			Percent retention			
Tensile at yield	Machine	2570 psi	109	105	107	109
	Transverse	2700 psi	104	102	101	110
Elongation at yield	Machine	19%	79	84	100	79
	Transverse	19%	84	79	95	74
Tensile at break	Machine	4080 psi	91	110	103	111
	Transverse	4040 psi	105	103	98	107
Elongation at break	Machine	810%	94	107	104	106
	Transverse	780%	105	104	100	106
Stress at 100% elongation	Machine	1790 psi	106	103	103	106
	Transverse	1840 psi	100	97	98	102
Stress at 200% elongation	Machine	1830 psi	104	102	103	103
	Transverse	1920 psi	97	96	96	98
Modulus of elasticity[c]	Machine	111,000 psi	92	96	116	120
	Transverse	118,500 psi	95	100	101	106
Tear strength	Machine	795 ppi	101	104	100	105
	Transverse	785 ppi	101	104	100	103
Puncture resistance[d]			Test values			
Thickness, mil		60.8	63.8	65.0	65.0	64.3
Maximum stress, lb		91.7	95.6	100.9	97.7	98.8
Elongation at puncture, in.		0.59	0.53	0.63	0.56	0.61
			Percent retention			
Stress normalized for 100-mil sheet		151 lb	99	103	99	102
Hydrostatic burst resistance			Test values			
Thickness, mil		64.7	62.9	66.0	63.0	63.9
Maximum stress, lb		557	565	569	550	580
			Percent retention			
Stress normalized for 100-mil sheet		861 psi	104	100	101	105
			Change in points			
Hardness, Duro D points 5-second reading		60	-3	-1	-2	-2

[a] The immersion liquid was deionized water spiked with the following: 1,1,1-trichloroethane, trichloroethylene, benzene, toluene, ortho-, meta- and para-xylenes, acetone, methyl ethyl ketone, di(ethylhexyl) phthalate, and tri-butyl phosphate.

[b] Matrecon identification number 392.

[c] Measured using 0.5 x 8-in. strip specimens with an initial jaw separation of 4.0 in. and an initial strain rate of 0.1 in./in. min. Using a specimen with a 10-in. gage length as specified in ASTM D882-83 would result in higher values.